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AN INTERMEDIATE COURSE OF
LABORATORY WORK IN CHEMISTRY

AN INTERMEDIATE COURSE

OF

LABORATORY WORK IN CHEMISTRY

BY

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WITH ILLUSTRATIONS

LONGMANS, GREEN, AND CO.

INTRODUCTORY NOTE

THE course of work given in the following pages has been built up gradually, and is the outcome of experience in preparing classes for the London Intermediate Science Examination. The book has been in use in manuscript form for three years, and all the preparations and analytical processes have been extensively tested in actual practice by students of very varied ability, the experience so obtained suggesting various modifications in detail which are now incorporated.

The ground covered is, broadly, that of the Intermediate Science (London), but it is not suggested that students preparing for that examination should perform all the experiments. On the contrary, a sufficiently large number has been given to enable the teacher to make a selection, and still have fresh experiments for a revision course. Honours students may attempt more preparations, and a larger variety of the volumetric and gravimetric exercises.

Further, the Authors hope that the course will be of service for other classes whose work is above matriculation standard, and are encouraged in this hope by the fact that much of the book has been used in the preparation of candidates for the Honours Examination in Chemistry conducted by the Welsh Central Board.

It has been assumed throughout that the student is not working by himself, but can obtain the advice and assistance of a teacher at all times.

Considerable care has been taken in compiling the index to facilitate reference, and also to give some indication of important general reactions and principles. The illustrations, which have

been inserted for the guidance of students in fitting up the more complicated apparatus, are reproductions of photographs which, in most cases, were taken during the progress of the respective experiments. Every part of the book has been carefully revised for the press, and the Authors hope that error of a serious nature has been avoided.

We should like to express our thanks to Mr. M. M. Pattison Muir and to Dr. J. K. H. Inglis for their helpful suggestions and criticisms.

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E. K. HANSON.

J. W. DODGSON.

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UNIVERSITY COLLEGE,
    READING,
        August, 1908.

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OF LABORATORY WORK
IN CHEMISTRY

ACTION OF THE HALOGENS ON THE HYDROXIDES OF THE METALS OF THE ALKALI AND ALKALINE-EARTHS.

I. THE action of chlorine on caustic potash.

The apparatus shown in Fig. 1 will be found convenient: the chlorine, obtained by the action of hydrochloric acid on manganese dioxide, is dried by passing through concentrated sulphuric acid, and led into the solution by means of an inverted funnel. In this way fairly complete absorption of the chlorine is ensured, and any sucking back of the liquid can be stopped by raising the funnel just clear of the surface, when the solution which may have entered the funnel will fall back into the beaker.

A. Action on cold dilute potash.

Into a beaker of about 500 c.c. capacity place 200 c.c. of a 5 per cent. solution of caustic potash, and pass the chlorine through the solution until the weight has increased by 5 grams; the temperature of the liquid should not be above 30° nor lower than 25°. The exact increase in weight must be carefully noted.

Estimate the amount of chlorine present as hypochlorite by the method given on p. 69.

What becomes of the rest of the chlorine?

B. Action on hot concentrated potash.

In 100 c.c. of water dissolve 50 grams of pure caustic potash,

and pass chlorine through the heated solution until no more chlorine is absorbed. Pour off a few c.c. into a weighed crucible, and evaporate to dryness on a water bath; weigh the residue, estimate the potassium chloride by the method given on p. 73, and subtract this weight from that of the total residue. The difference is the weight of potassium chlorate present. From the results of your experiment, deduce an equation expressing the chemical reaction. Allow the rest of the solution to cool, and
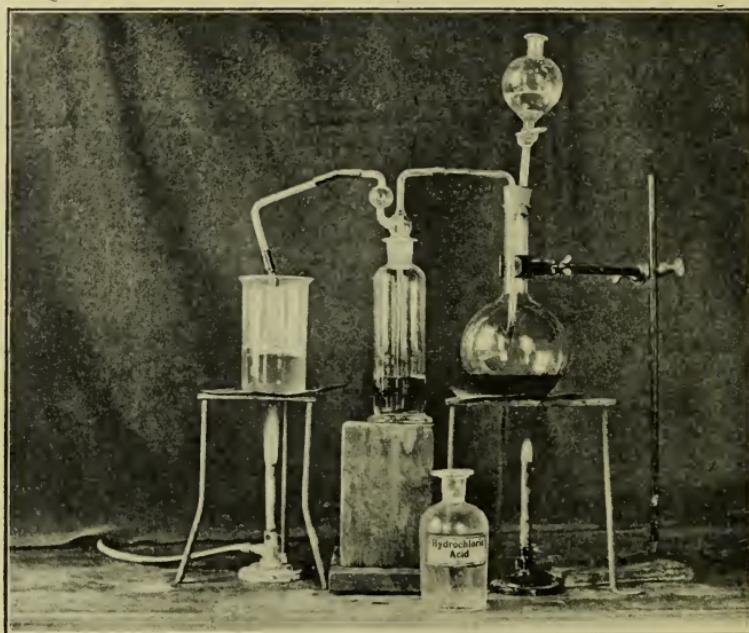
FIG. 1.

pour off the mother liquor from the crystals; wash them two or three times with cold water by decantation, then re-crystallise by dissolving in a small quantity of hot water, and again allowing to cool.

II. The action of chlorine on lime.

This can be investigated in a precisely similar manner to the above, using a "cream" of lime in place of potash solution.

Exercises.—The student should devise modifications of the process such as to enable him to examine some of the following cases :—

Action of chlorine on caustic soda, or baryta.

Action of bromine on caustic potash, soda, lime, or baryta.

Action of iodine on caustic potash, soda, lime, or baryta.

PREPARATION OF CHLORIC ACID.[1]

Dissolve 20 grams of barium chlorate [$Ba(ClO_3)_2 . H_2O$] in 100 c.c. of water ; heat to boiling, and add 25 c.c. of 5N * H_2SO_4. Allow to stand, and decant off the clear liquid. Concentrate the solution in vacuo at the ordinary temperature until signs of decomposition can be perceived.

The product is a yellowish liquid of powerful oxidising properties ; it must not be warmed, as it decomposes with explosion at about 40° C.

Drop a couple of drops on filter paper, and note the effect. Neutralise the diluted acid with sodium carbonate, and crystallise out the sodium chlorate.

Why is the barium salt selected for this preparation ?

PREPARATION OF POTASSIUM PERCHLORATE.

Heat in a nickel crucible 15 grams of potassium chlorate which has been finely powdered. The substance first melts, and then commences to give off oxygen with effervescence. After some time the melt, which should be constantly stirred, will become pasty ; the heating should now be stopped, the crucible allowed to cool, and the contents dissolved in hot water, the smallest possible quantity being used ; the solution is allowed to cool, and the precipitated perchlorate purified by re-crystallisation.

A small portion of the salt should be tested with concentrated sulphuric acid ; the presence of undecomposed chlorate is indicated by the evolution of chlorine peroxide (Explosive !).

[1] *This experiment should be performed* **only** *by more experienced students.*

* For meaning of this symbol see p. 47.

Potassium perchlorate, $KClO_4$, crystallises in transparent rhombic prisms which contain no water of crystallisation.

Solubility in cold water is very small, and a solution of sodium perchlorate can be used as a reagent for potassium. M.pt. $610°$ C.; decomposition commences about $400°$ C., before fusion. M.pt. of potassium chlorate, $334°$ C.; decomposition pt. $352°$ C.

Exercise.—Heat potassium nitrate, identify any gas evolved and examine the residue by the table for detection of acids (p. 99).

PREPARATION OF IODINE PENTOXIDE.

Heat gently in a round-bottomed flask 15 grams of iodine with 60 c.c. of fuming nitric acid; the heating must be so regulated that no considerable loss of iodine takes place. Add more fuming nitric acid if necessary for the complete oxidation of the iodine. The contents of the flask should be transferred to an evaporating basin, and concentrated till crystallisation begins. The crystals of iodic acid so obtained are drained and dried on a porous tile, and then heated gently in a porcelain crucible until the weight is constant.

Iodine pentoxide, I_2O_5, is a white amorphous powder; it is decomposed above $300°$ C. into iodine and oxygen. With water it gives iodic acid. It is very slightly soluble in alcohol.

Iodic acid, $H_2I_2O_6$, is dehydrated at $170°$ C., giving iodine pentoxide. It is very slightly soluble in alcohol; very soluble in water.

Both are very energetic oxidising agents.

Exercise.—From the iodic pentoxide, prepare specimens of calcium and potassium iodates, and compare the action of heat on them.

[Compare also exercises on p. 3.]

PREPARATION OF OXYGEN FROM BLEACHING POWDER BY MEANS OF A COBALT SALT.

Fit a flask of half a litre capacity with thistle funnel and delivery tube. In the flask place 250 c.c. of a solution of bleaching powder, made in the cold, by grinding it in a mortar with sufficient water to make a thin cream, diluting and filtering. Add two or three drops of a solution of cobalt chloride; the addition of the cobalt chloride causes the formation of a black
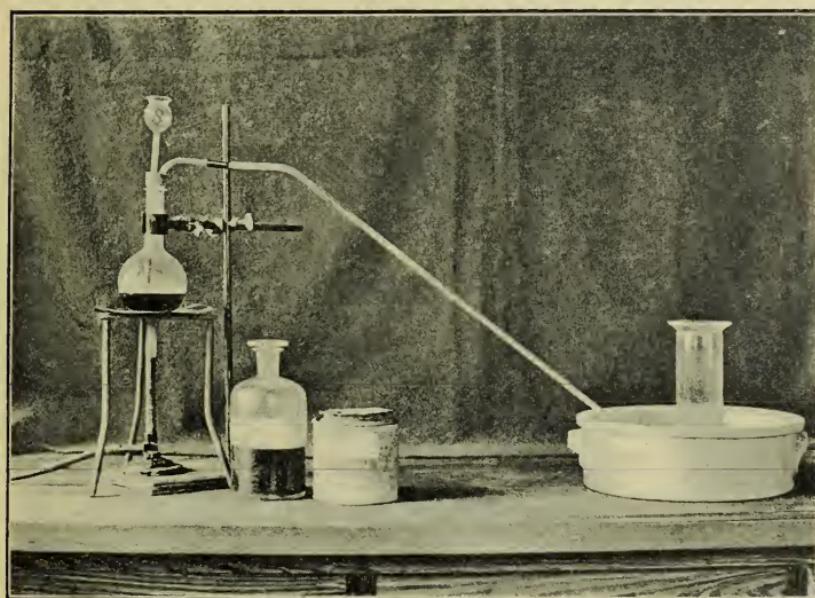
Fig. 2.

precipitate. Heat gently; oxygen is given off with brisk effervescence. Fresh bleaching powder solution may be added through the thistle funnel as required. Collect the gas over water.

With what other instances of catalytic action are you acquainted?

PREPARATION OF FERROUS SULPHATE.

Place 10 grams of iron wire in a flask of about 300 c.c. capacity, fitted with a perforated cork; pour 100 c.c. of diluted sulphuric acid (1:7) on to the iron, and heat gently until the whole of the iron is dissolved. Filter the cooled solution rapidly into a beaker, and add alcohol in amount equal to the volume of the solution. Allow to settle; decant off the liquid, wash the precipitate on to a filter paper with alcohol, and wash two or three times with alcohol. Transfer to a porous tile, and dry until the crystals cease to cohere.

Ferrous sulphate, $FeSO_4.7H_2O$, is practically insoluble in alcohol. It normally crystallises in monoclinic crystals.

Exercise.—Compare the effect of adding alcohol to a concentrated solution of calcium chloride.

PREPARATION OF FERROUS AMMONIUM SULPHATE.

Weigh out carefully 27·8 grams of pure crystallised or granulated ferrous sulphate, and 13·2 grams of pure ammonium sulphate, and dissolve each salt separately in the least possible quantity of distilled water at a temperature of about 40° C. (If the solutions are not perfectly clear they must be filtered.) Mix them together at the same temperature in a porcelain dish, adding one or two drops of pure concentrated sulphuric acid, and stir till cold. During the stirring, the crystalline double salt will separate out in a fine granular form. Set aside for a few hours, pour off the supernatant liquid, drain and dry the crystals at the ordinary temperature.

From the mother liquor, a further supply of larger crystals can often be obtained on allowing it to stand.

The salt is a convenient one for standardising solutions of potassium permanganate or dichromate, as it contains exactly one-seventh of its weight of iron, and is much less readily oxidised than simple ferrous salts; the granular form should be used (see p. 59).

Ferrous ammonium sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, crystallises in pale green monoclinic prisms; solubility at 36° C. is 31·8 in 100 of water, and at 12° C., 17·5 in 100.

Note.—For other double sulphates of this type, see p. 37.

PREPARATION OF IRON AMMONIUM ALUM.

Into a beaker put 27·8 grams of powdered crystallised ferrous sulphate, and dissolve with the aid of heat in about 50 c.c. of water, adding not more than 5 c.c. of concentrated sulphuric acid. Add concentrated nitric acid drop by drop, until the black coloration first produced disappears with liberation of nitric oxide, · and a clear red brown liquid is obtained. Add to the solution 6·6 grams of ammonium sulphate, previously dissolved in a small quantity of water, and filter if necessary. Allow to stand and crystallise.

Iron ammonium alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, crystallises in octahedra of a pale violet colour, isomorphous with the other alums. At about 150° C. it loses 23 molecules of water; the remaining molecule is not driven off until a temperature of 230° C. is reached. Solubility: 20 in 100 at 15° C.

Note.—For other alums see pp. 13 and 36.

Exercise.—The student may estimate the amount of iron in this salt by one of the methods described on pp. 60, 64, 83.

PREPARATION OF POTASSIUM PERMANGANATE.

Fuse together in an iron dish 30 grams of potassium hydroxide, 8 grams of potassium chlorate, with the addition of 10 c.c. of water. When the fusion is complete, add gradually 40 grams of finely powdered pyrolusite. The mixture should be constantly stirred, but not heated while the pyrolusite is being added. When this process is completed, heat the mixture until it is quite dry, transfer to a flask of about two litres capacity, and add about a litre of water.

The flask should be fitted with a cork, through which three

glass tubes pass, two of them dipping below the surface of the water in the flask.   One of these must be connected with an apparatus supplying carbon dioxide; the other one is open to the air.   The remaining tube, which must be well above the surface of the liquid, is connected to a water pump.

Boil the contents of the flask, and by means of the pump draw carbon dioxide and air through the liquid; continue the process until a drop of the liquid gives a pure pink colour when dropped on filter paper.   Filter the contents of the flask through glass wool, and evaporate the clear liquid until crystals form on cooling.   Purify by recrystallisation from water.

Potassium permanganate, $KMnO_4$, crystallises in dichroic rhombic prisms, isomorphous with potassium perchlorate; it imparts an intense violet-red colour to its aqueous solutions. Solubility : $6\frac{1}{2}$ in 100 in cold water.

PREPARATION OF POTASSIUM COBALTI-NITRITE (COBALT YELLOW)

Dissolve 16 grams of potassium nitrite in 20 c.c. of water in a beaker.   In a separate beaker prepare a solution of 4 grams of crystallised cobaltous chloride in 20 c.c. water, and acidify with 15 c.c. of glacial acetic acid.   Add the solution of potassium nitrite carefully to the cobalt solution : a vigorous reaction, with evolution of nitric oxide, takes place, and a yellow precipitate will settle to the bottom of the liquid.   Filter, wash, and dry. Potassium cobalti-nitrite, $K_6Co_2(NO_2)_{12}$, is a bright yellow micro- crystalline substance : it is slightly dissociated by pure water.

Note that excess both of acetic acid and of nitrite is necessary, as the nitrous acid acts as an oxidising agent on the cobaltous salt.   What is the usual action of nitrous acid?

Note.—Nickel salts, when treated as above, give no precipitate, and there- fore the formation of the insoluble cobalti-nitrite can be used as a means of separating cobalt from nickel.   The student is advised to try this method of separation.

The reaction also serves as a test for potassium (see p. 116).

PREPARATION OF SODIUM THIOSULPHATE.

Dissolve 25 grams of powdered sodium sulphite in water ; use only clear crystals. The solution can best be effected by grinding up the sodium sulphite in a mortar with cold water, allowing to stand and decanting off the clear liquid. Several repetitions of this process will ensure complete solution without the aid of heat. Filter the solution, if necessary, and boil with flowers of sulphur until no more sulphur dissolves ; again filter, evaporate to small volume and allow to crystallise. Purify by re-crystallisation.

Sodium thiosulphate, $Na_2S_2O_3.5H_2O$, forms clear monoclinic crystals terminated by short pyramids. It melts in its own water of crystallisation at 48° C.

Exercises. —1. Examine the action of the following substances with a solution of the salt :—dilute hydrochloric acid, iodine solution, silver nitrate solution, silver chloride, and solution of potassium permanganate.

2. Melt some sodium thiosulphate in a large test-tube, using as much of the salt as will, when melted, half fill the tube. Allow to cool, and notice that the salt does not solidify. Drop in a small crystal of the solid, and observe—

(*a*) change of state,
(*b*) alteration of temperature.

PREPARATION OF SULPHUR TRIOXIDE.

(i) Into a small stoppered glass retort carefully pour fuming (Nordhausen) sulphuric acid [1] until the retort is about one-third full. Gently warm the liquid with a small flame ; white fumes of sulphur trioxide will be evolved, which will condense in the lower part of the retort. A dry receiver should be provided to prevent the escape of any of the sulphur trioxide.

(ii) Arrange an apparatus as shown in the accompanying diagram :—apparatus for the generation of sulphur dioxide ; gas holder containing oxygen ; wash bottle containing concentrated

---

[1] This acid is a solution of sulphur trioxide in sulphuric acid, and may be looked upon as containing $H_2S_2O_7$, pyrosulphuric acid.

sulphuric acid for drying the gases; combustion tube containing platinised asbestos; receiver immersed in cold water.

Pass a current of sulphur dioxide through the sulphuric acid in the wash bottle, where it is also mixed with oxygen from the gas holder. Lead the two gases, mixed in about equal proportions, over the platinised asbestos heated gently in the combustion tube. In the presence of the platinum the two gases combine,
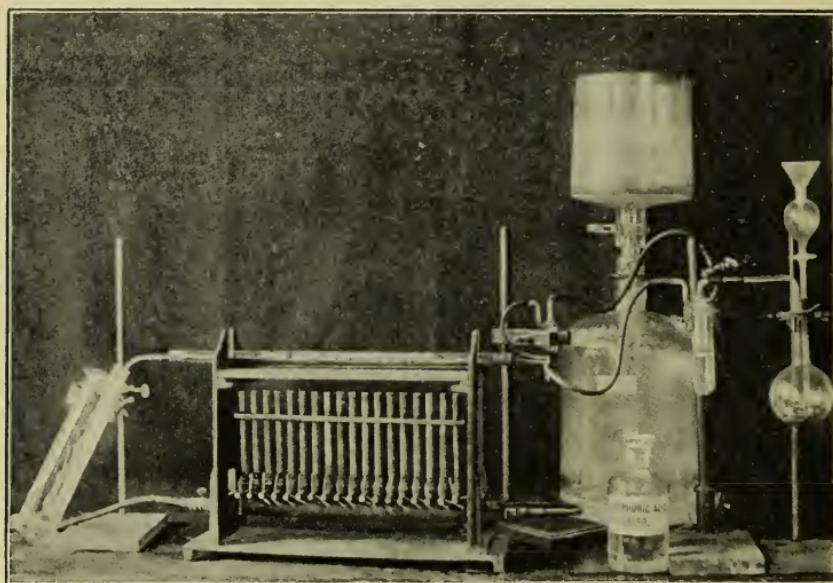
Fig. 3.

and sulphur trioxide is formed, which will be carried out by the current of gas, and deposited in the receiver.

Sulphur trioxide, SO_3, is a white crystalline substance which acts very energetically upon water; is absorbed by concentrated sulphuric acid to form pyrosulphuric acid, and dissociates on being heated to a high temperature.

Note.—Preparation of platinised asbestos. Soak good fibrous pieces of asbestos in a fairly strong solution of platinic chloride, and then hold each piece separately in a Bunsen flame, until the chloride is completely decomposed, and a dark grey deposit of platinum is left on the asbestos. The platinised asbestos thus prepared should glow brightly when held in a stream of coal-gas, issuing from a Bunsen burner. Repeat the treatment with platinic chloride and subsequent heating, if necessary.

PREPARATION OF POTASSIUM PYROSULPHATE.

Heat seven grams of potassium hydrogen sulphate in a porcelain crucible as long as water is given off; the action must be stopped at the first sign of any evolution of white fumes. Dissolve the residue in the smallest possible quantity of hot water (excess of water decomposes the salt). Allow to crystallise by cooling. Drain the crystals, and dry on a porous tile.

Potassium pyrosulphate, $K_2S_2O_7$, crystallises in colourless needles.

What is the effect of continued heating on this salt?

PREPARATION OF POTASSIUM CHROMATE FROM CHROME IRON ORE.

Take 20 grams of finely powdered chrome iron ore, and thoroughly mix with 60 grams of dry potassium carbonate, and 40 grams of powdered nitre. Place the whole in an iron crucible of at least 100 c.c. capacity, and heat strongly over the blow-pipe flame until the oxidation of the chromium is completed, as shown by the orange colour of the fused material. Allow to cool, and extract the residue with boiling water; filter, crystallise, and purify the potassium chromate by re-crystallisation.

Potassium chromate, K_2CrO_4, forms lemon-yellow rhombic crystals, isomorphous with potassium sulphate. Solubility 62·94 in 100 at 20° C.; 79·19 in 100 at 100° C.

Note.—Chrome iron ore may be regarded as $FeO.Cr_2O_3$. The attention of the student is called to the difference in the action of oxidising agents in the presence of alkali upon the oxide of iron and the oxide of chromium; the ferrous oxide is merely oxidised to ferric oxide, which will not combine with alkali, but forms the chief constituent of the insoluble residue, a separation of the iron from the chromium being thus effected.

PREPARATION OF CHROMIUM TRIOXIDE

Take 40 c.c. of a cold saturated solution of potassium dichromate, and add 60 c.c. of concentrated sulphuric acid slowly, with constant stirring. Allow the deep red liquid to cool slowly. Long needle-shaped crystals of chromium trioxide will separate out. Decant off the excess of liquid, wash three or four times by

decantation with successive very small quantities of concentrated nitric acid. Drain the crystals on a perforated plate as rapidly as possible by the aid of the pump, finish drying upon a porous tile, place in a test tube and hermetically seal **Avoid the use of filter paper.**

Chromium trioxide, CrO_3, crystallises in red, slender rhombic needles; it is extremely soluble in water. It is decomposed instantly with explosive violence on contact with alcohol; it decomposes on being heated, giving chromium sesquioxide and oxygen.

To a very dilute aqueous solution of chromium trioxide in a test tube add a little hydrogen peroxide, and then a layer of ether, and shake. The ether extracts a deep blue unstable compound (perchromic acid) which readily evolves oxygen with effervescence.

PREPARATION OF CHROMYL CHLORIDE.

Mix together 30 grams of powdered potassium dichromate and
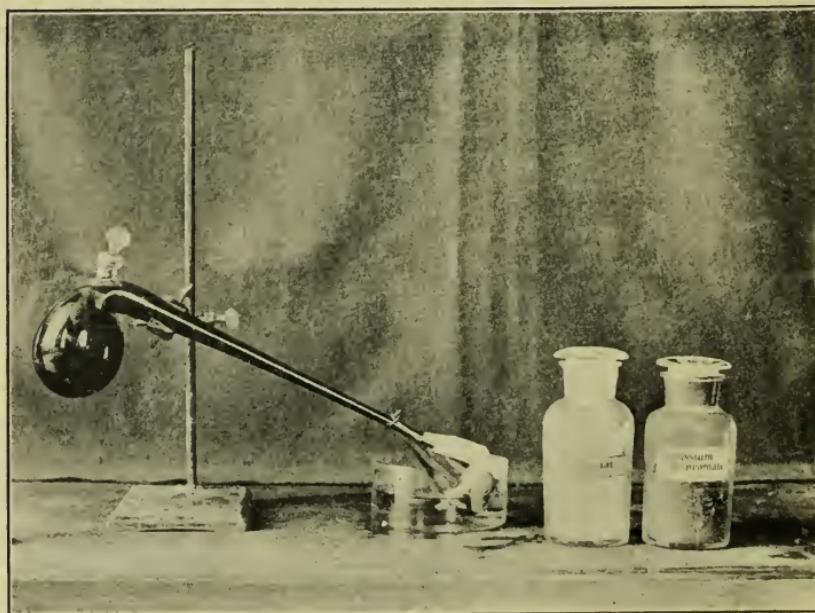
FIG. 4.

20 grams of sodium chloride—note that both substances must be

perfectly dry. Introduce the mixture into a dry stoppered retort of about 250 c.c. capacity, and add 80 c.c. of concentrated sulphuric acid. Heat cautiously; red vapour is given off, which condenses to a deep red liquid in the cooler part of the retort, and should be collected in a dry receiver cooled by ice-water. Allow this liquid to stand for a day or so: pour off the liquid and redistil from a small retort.

Chromyl chloride, CrO_2Cl_2, is a deep red liquid which fumes in the air; B.pt., $116°$ C.; sp. gr., $1·9$ at $25°$ C. It is a powerful oxidising agent.

Exercise.—Examine the action of water on the liquid (see p. 105.)

PREPARATION OF CHROMIUM SESQUIOXIDE.

Dissolve 15 grams of potassium dichromate in 150 c.c. of water, and add gradually 12 c.c. of concentrated sulphuric acid. To the mixture, which should be kept at a temperature of about $30°$ C., add, very slowly, alcohol until reduction is complete, as indicated by a drop giving a pure green colour when placed on a piece of filter paper. Boil off the aldehyde (readily recognised by its odour) and the excess of alcohol, and add ammonia in slight excess, and again boil to remove the excess of ammonia. Filter off the precipitate, wash thoroughly, dry, and ignite.

Chromium sesquioxide, Cr_2O_3, is an amorphous green powder, which becomes brownish on being heated strongly. The colour varies with the method of preparation.

The ignited oxide is only soluble with great difficulty in acids.

Exercise.—Prepare chromium sesquioxide—
(1) By heating a few crystals of ammonium dichromate.
(2) By heating mercurous chromate.
What is the nature of the decomposition in each of these cases?

PREPARATION OF CHROME ALUM.

Proceed as in the preparation of chromium sesquioxide to the point of complete reduction of the chromium, when instead of adding ammonia the solution should be evaporated to small bulk

and allowed to crystallise. The solution will be deep green in colour, and several days will elapse before crystallisation commences, but ultimately violet crystals, isomorphous with the other alums, will be deposited.

Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, crystallises in octahedra belonging to the cubic system. It is soluble in about six parts of cold water.

Note.—For other alums see pp. 7 and 36.

PREPARATION OF CHROMOUS ACETATE.

Boil together in a beaker in the fume cupboard 400 c.c. of concentrated hydrochloric acid and 40 grams of chromium trioxide.
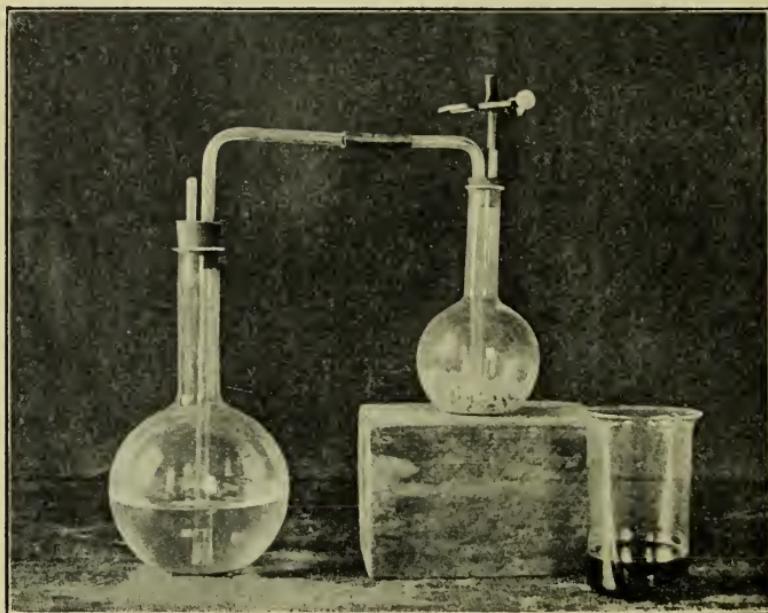
FIG. 5.

Continue the heating until chlorine ceases to be given off, and the liquid has become dark green in colour. Reduce the volume of

the solution by evaporation to about 150 c.c., and then pour it upon 200 grams of granulated zinc contained in a large flask, fitted as shown in the figure. Do not insert the cork until the energy of the reaction has somewhat subsided : the clip should not be on the tube until it is required. The second flask contains 320 grams of sodium acetate dissolved in 1200 c.c. of water. The reducing action of the nascent hydrogen produced by the action of the zinc on the hydrochloric acid causes the chromic chloride to change into chromous chloride, the formation of which is accompanied by a change in the colour of the solution from green to brilliant blue. When a good blue colour is obtained, close the tube by means of the clip ; the pressure of the hydrogen evolved in the first flask will then force the solution of chromous chloride into the second flask, and chromous acetate will be precipitated as a dark purple-red crystalline powder. Wash the precipitate several times with water which has been boiled for some minutes, rapidly cooled, and saturated with carbon dioxide ; drain the precipitate as much as possible, transfer the paste to a tube, and seal up the tube in a blow-pipe.

PREPARATION OF ANHYDROUS CHROMIUM CHLORIDE.

Prepare a *stiff* paste of green oxide of chromium and concentrated sugar syrup, and make it into small lumps about the size of peas; place the pieces in a covered nickel crucible, and heat until the sugar is completely carbonised. Transfer to a hard glass tube open at both ends, pack loosely, taking care not to fill the tube for more than half its length. Put the tube on a combustion furnace ; connect the end of the tube nearest the mixture with an apparatus for supplying *dry* chlorine, raise the temperature to red heat, and then pass a fairly rapid current of chlorine over the mixture. Do not heat the portion of the tube not occupied by the mixture. Anhydrous chromium chloride, $CrCl_3$, will sublime on to the cool part

of the tube in bright heliotrope-coloured crystals. It is insoluble in
acids, but is decomposed by fusing with caustic alkalis, or alkaline
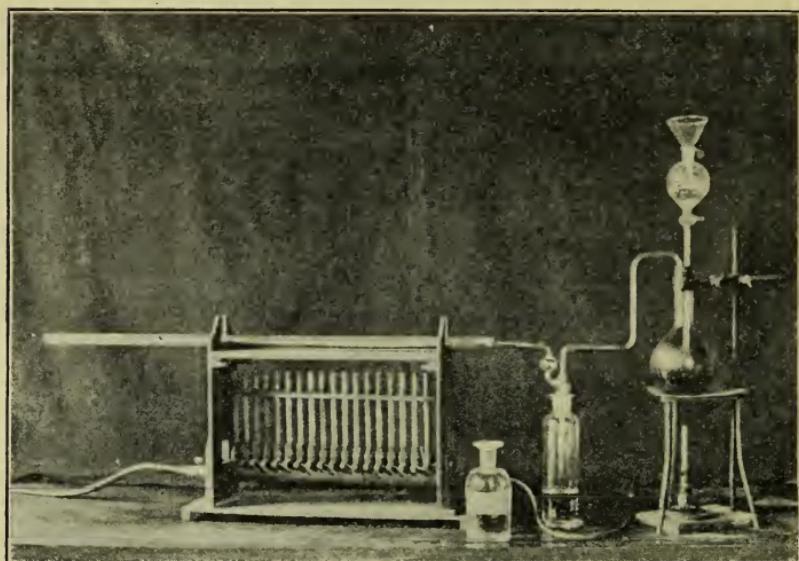
FIG. 6.

carbonates. It dissolves in water containing a very small trace of
stannous chloride.

PREPARATION OF SILVER HYPONITRITE.[1]

To a solution of 10 grams of sodium nitrite in 35 c.c. of water,
add slowly 250 grams of sodium amalgam (containing about
3 per cent. of sodium) keeping the solution cold by small pieces
of ice. When hydrogen bubbles cease to be evolved, decant off
the liquid from the mercury into a beaker, and neutralise with
acetic acid. Add silver nitrate to the solution as long as a
precipitate is produced, and allow the mixture to stand in good
daylight, *but not in direct sunshine*, for a few hours, when the
silver acetate which is usually contained in the precipitate will be
decomposed with formation of silver. Dissolve the silver

---

[1] *This experiment should be performed* **only** *by more experienced students.*

hyponitrite out of the precipitate with very dilute sulphuric acid, filter, and reprecipitate the silver hyponitrite with very dilute ammonia, *which must not be added in excess.* Filter with the aid of a pump, wash with small quantities of ice-cold water, and dry in a sulphuric acid desiccator under diminished pressure. All solutions must be cooled by ice, and direct sunlight must be avoided.

Silver hyponitrite, $Ag_2N_2O_2$, is a yellow substance very slightly soluble in water. It is stable at ordinary temperatures; it commences to decompose at 100° C.; at 150° C. the decomposition is rapid, but not explosive if the salt is pure. The products of decomposition are said to be silver, nitrogen, nitric oxide, and nitrogen peroxide.

PREPARATION OF PHOSPHORUS TRICHLORIDE.

Cover the bottom of a retort with a fairly thick layer of sand,
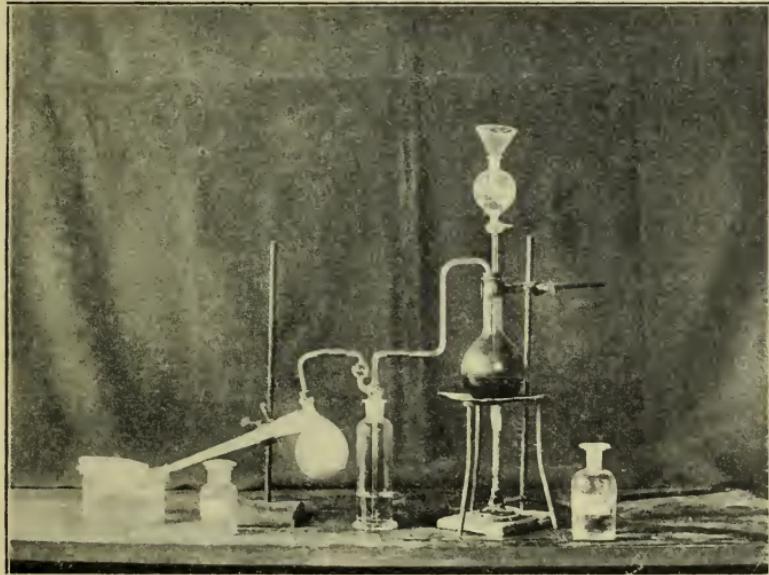
FIG. 7.

freed from moisture and organic matter by ignition. Fit into the tubulus of the retort a cork perforated with one hole, through

C

which a glass tube passes loosely. Displace the air in the retort by dry carbon dioxide, and then introduce 20 grams of white phosphorus cut into small pieces under water, and carefully dried (each piece should be taken out of the water separately with a pair of pincers and dried on filter paper).

Connect the tube to an apparatus supplying dry chlorine, and pass a fairly rapid current of the gas over the phosphorus. The phosphorus begins to burn with a faintly luminous flame, and phosphorus trichloride will condense in the neck of the retort, and may be collected in a thoroughly dry and well-cooled receiver. Purify by redistillation.

The formation of the trichloride may be controlled by altering the position of the tube in the cork ; if the current of chlorine is too rapid, the heat generated may be so great as to cause distillation of phosphorus, or even the formation of red phosphorus ; the tube should then be slightly withdrawn. If withdrawn too far, however, the chlorine may remain too long in contact with the phosphorus, and cause the formation of phosphorus pentachloride, which will condense as a solid on the retort.

Phosphorus trichloride is a colourless liquid which fumes in air, and is decomposed by cold water, yielding phosphorous and hydrochloric acids. B.pt., 78° C.

Phosphorus is soluble in phosphorus trichloride.

What is the action of phosphorus trichloride on alcohols, and on fatty acids ?

PREPARATION OF BARIUM HYPOPHOSPHITE.

In a flask of half a litre capacity, place 250 c.c. of water, 5 grams of yellow phosphorus weighed under water in a small beaker, and 30 grams of crystallised barium hydroxide. Fit the flask with a two-holed cork ; through one of the holes pass a delivery tube, one end of which should come just through the cork, and the other dip just under the surface of water in a trough. Through the other hole in the cork pass a glass tube, one end of

which should dip below the liquid in the flask, and the other
end be connected with a gas supply. Pass a stream of coal gas
through the apparatus to drive out all the air, and then commence
to heat the flask and its contents. Continue the heating as long
as phosphine is evolved. Then drive out the phosphine remaining
in the apparatus by a current of coal gas; allow the liquid to cool
thoroughly, and disconnect from the gas supply. Substitute an
apparatus for the production of carbon dioxide, and pass a rapid
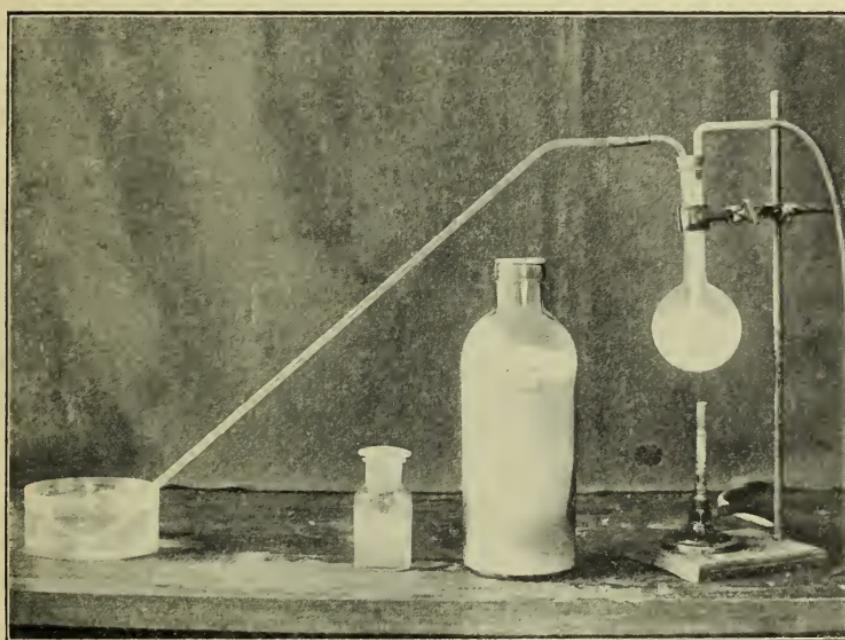
Fig 8.

current until the solution is no longer alkaline to litmus paper.
Filter the contents of the flask, and concentrate the filtrate on the
water bath until crystals are formed. Collect the crystals, and
dry them on a tile.

Barium hypophosphite, $BaH_4P_2O_4.2H_2O$, crystallises in needles,
which lose their water of crystallisation at $100°$ C. It is nearly
as soluble in cold as in hot water, the solubility being about
30 in 100.

PREPARATION OF PHOSPHORIC ACID.

Place 5 grams of red phosphorus in a flask of about half a litre capacity. Cover with water, add concentrated nitric acid to a depth of half an inch, and warm gently until the action commences. When the action has once started, it will proceed without further heating. When all the phosphorus has dissolved, transfer to an evaporating basin, and drive off the nitric acid. Dilute the syrupy residue with water, filter, and again evaporate at a temperature not exceeding 200° C. Repeat if necessary. A clear syrupy liquid should be the final product. The experiment should be carried out in a fume cupboard.

Ortho-phosphoric acid, H_3PO_4, usually remains liquid when prepared as above, but can be obtained in rhombic crystals melting at 41° C.

What is the action of heat on ortho-phosphoric acid? By what means is phosphorus obtainable from the residue?

PREPARATION OF THE THREE PHOSPHATES OF SODA.

Dissolve 30 grams of syrupy phosphoric acid in water, and divide the solution into three equal portions. Neutralise one portion with a solution of caustic soda, using litmus paper as indicator,[1] and crystallise the disodium hydrogen phosphate so formed.

To the second portion of the phosphoric acid solution, add half the quantity of the same caustic soda solution as was used in the first instance, and crystallise the dihydrogen sodium phosphate.

To the remaining portion of the phosphoric acid add three times the amount of caustic soda solution used in the second experiment, and crystallise the tri-sodium phosphate.

[1] The paper should not be placed in the solution, but the end of a glass rod should be just dipped in the solution from time to time, and the red litmus paper touched with the damp rod.

Disodium hydrogen phosphate, $Na_2HPO_4 . 12H_2O$, crystallises in monoclinic prisms which are efflorescent. Solubility : 3 parts of anhydrous salt in 100 of cold water, 96 in 100 of hot water.

Sodium dihydrogen phosphate, $NaH_2PO_4 . H_2O$, crystallises in rhombic prisms : very soluble in water.

Trisodium phosphate, $Na_3PO_4 . 12H_2O$, crystallises in hexagonal prisms. Solubility : 4 parts of anhydrous salt in 100 of water at 10° C., 108 in 100 of water at 100° C.

Exercise. Examine the action of silver nitrate on each of these salts in aqueous solution.

What is the action of heat on each of these substances ?

PREPARATION OF ARSENIC PENTOXIDE AND NITROGEN TRIOXIDE.

Place 10 grams of white arsenic in a flask of about half a litre
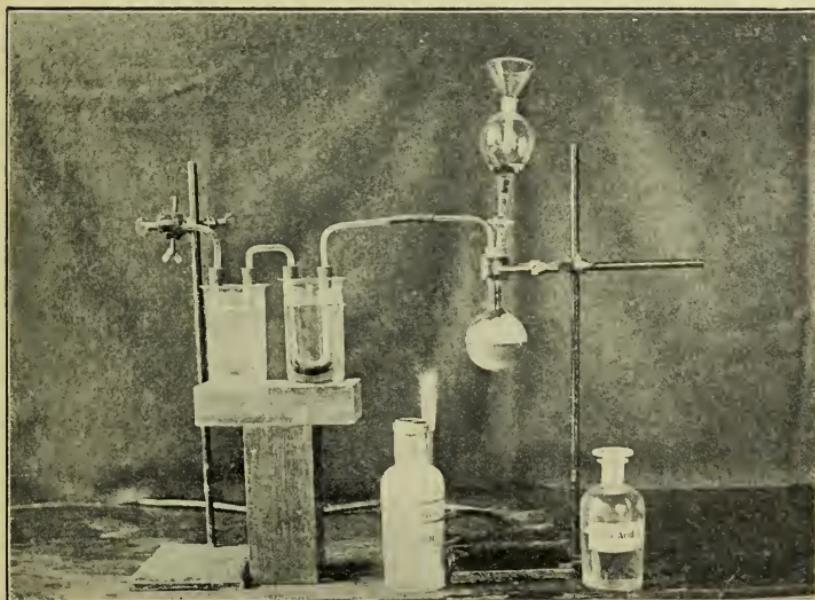
FIG. 9.

capacity. Fit the flask with a thistle funnel and delivery tube ; the delivery tube is connected to a **U**-tube immersed in cold

water, and this in turn to a second **U**-tube immersed in a mixture
of ice and salt. Add 50 c.c. of nitric acid of sp. gr. 1·3 through
the thistle funnel, and warm gently; a red gas is given off, which
condenses in the second **U**-tube to a deep blue liquid, any nitric
acid which is carried over being condensed in the first tube. The
blue liquid is mainly nitrogen trioxide; it cannot be preserved at
ordinary temperatures.

Pour the contents of the flask into an evaporating basin, drive
off the excess of nitric acid, and heat the residue strongly. A
white amorphous powder (arsenic pentoxide) will be left. Dis-
solve some of this in water, and test for arsenic acid.

Note.—Compare preparations on pp. 4 and 20.

PREPARATION OF ANTIMONY TRICHLORIDE.

In a 500 c.c. flask heat 50 grams of black antimony sulphide
with 250 c.c. of concentrated hydrochloric acid, adding a few
grams of powdered potassium chlorate in small quantities at a
time. When solution is complete, filter off any insoluble residue
through glass wool, and distil from a retort. Test the liquid
distilling over from time to time by allowing a few drops to
fall into water; as soon as a white precipitate is obtained change
the receiver. Once more test the distillate at intervals by letting
a little cool on a clean glass rod, and when the distillate begins
to solidify on a glass rod collect in a fresh receiver. Antimony
trichloride will now solidify in the receiver.

Antimony trichloride, $SbCl_3$, is a crystalline mass; m.pt.,
73·2° C.; b.pt., 223·5° C.

PREPARATION OF "POWDER OF ALGAROTH."

The second portion of the distillate in the above experiment
(which gave a white precipitate with water) should be poured into
half a litre of water, and allowed to stand for some days. The
precipitate will then have become crystalline, and can be readily
filtered, washed, and dried.

Exercise.—Prepare antimony pentachloride by passing chlorine through the trichloride melted in a small flask immersed in boiling water.

Antimony pentachloride, $SbCl_5$, is a yellow fuming liquid which solidifies in a freezing mixture at $-6°$ C.; it decomposes on distillation at the ordinary pressure into chlorine and the trichloride. B.pt. at 22 mm. is $79°$ C.

PREPARATION OF BASIC BISMUTH NITRATE.

Place in a beaker 10 grams of powdered bismuth nitrate, and add 150 c.c. of water, and boil until the whole of the precipitate has become converted to a white amorphous powder, which sinks rapidly to the bottom of the liquid. Filter, wash thoroughly, and dry in a steam oven.

PREPARATION OF BISMUTH PENTOXIDE.

Take the product of the previous experiment, and fuse with twice its weight of caustic potash in contact with the air, in an evaporating basin. Add a very small quantity of powdered potassium chlorate, and continue the heating until the mixture has turned red-brown in colour. Extract with boiling water, and throw the residue upon a filter in a funnel, wash first with dilute nitric acid, and finally with water. Dry in a steam oven.

Bismuth pentoxide, Bi_2O_5, has probably not been isolated in a pure state ; the composition of the substance obtained by the fusion in the above experiment is possibly $KBiO_3 . nBi_2O_5$. A good deal of the potash can be washed out by water saturated with carbon dioxide, but even dilute nitric acid appears to leave some of the bismuthate undecomposed.

PREPARATION OF FORMIC ACID.

Into a flask of about half a litre capacity, put 250 c.c. of pure glycerin and 40 grams of crystallised oxalic acid. Into the neck of the flask fit a cork with two holes. Through one hole insert a thermometer, the bulb of which is below the surface of the

liquid, and through the other a delivery tube connected with a condenser.

Heat the contents of the flask gently ; when the temperature reaches about 80° C. carbon dioxide will be given off.   Gradually raise the temperature to about 120° C. ; formic acid distils over and collects in the receiver.

This process may be repeated several times with the same glycerin, until a sufficient quantity of formic acid has been prepared (say 200 c.c.)

Dilute the distillate to about half a litre, divide into two portions, and add to one portion copper carbonate, and to the other lead carbonate (white lead), in small quantities, until no more is dissolved.   In each case assist the solution of the carbonate by gently heating.   Separate from the residue, and crystallise out the respective formates.

Formic acid, HCOOH, is a clear colourless liquid of penetrating odour.   B.pt., 100° C. The perfectly anhydrous acid solidifies on cooling below 0° C. ; the crystals so obtained melt at 8·6° C. Sp. gr., 1·23.   It mixes in all proportions with water, alcohol, or ether.

Copper formate, $Cu(HCOO)_2 . 4H_2O$, crystallises in blue monoclinic prisms.   It is easily soluble in water.

Lead formate, $Pb(HCOO)_2$, crystallises in small colourless needles.   Solubility : $2\frac{1}{2}$ in 100 of water at 15° C.

INTERACTION OF SULPHURIC ACID AND ALCOHOL.

Place in a flask of about a litre capacity 100 c.c. of absolute alcohol, and slowly add 100 c.c. of pure concentrated sulphuric acid, shaking after each addition, and cooling under the tap whenever necessary, as a considerable amount of heat is evolved.

The student will observe that the amounts of alcohol and sulphuric acid are approximately in the proportion (by mass) required by the equation,

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$
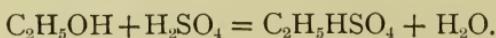
This action indeed takes place, but not completely. It is a so-called "reversible" reaction, water acting on ethyl hydrogen sulphate to give alcohol and sulphuric acid. It is subject to the "Law of mass action," and excess of alcohol will cause more complete transformation of the sulphuric acid into ethyl hydrogen sulphate. For this reason additional alcohol is added in preparation I., as the yield is thereby improved, and further, a large excess of sulphuric acid is not desirable, for this must be precipitated by calcium sulphate, as detailed below.

The student should refer to a text-book for further information on "reversible reactions" and the influence of mass.

I. Place 50 c.c. of the mixture in a flask of about 300 c.c. capacity and add 50 c.c. of alcohol. Attach a reflux condenser, and heat on a water bath for three hours. Allow the liquid to cool, and dilute to half a litre with cold water. Place the mixture in a large basin, and neutralise it by adding chalk ground up into a thin paste with water. The free sulphuric acid is precipitated as calcium sulphate, and the solution will contain calcium ethyl sulphate and free alcohol. Filter through calico, warm the filtrate, and add potassium carbonate solution, in small quantities, until the liquid is very slightly alkaline. The white precipitate produced is calcium carbonate : this must be removed by filtering through calico, and the clear filtrate concentrated until crystallisation commences on cooling.

Potassium ethyl sulphate, $KC_2H_5SO_4$, crystallises in thin colourless plates.

II. Use a round-bottomed flask of about half a litre capacity, and introduce a second 50 c.c. of the mixture of alcohol and acid, adding a further 50 c.c. of concentrated sulphuric acid. Fit the flask with a cork and delivery tube. Heat the mixture, avoiding over-heating, and consequent carbonisation, as much as possible, and collect the evolved ethylene over water. As a small amount of carbon is invariably formed, with reduction of the sulphuric acid, and liberation of sulphur dioxide, it is necessary to pass the gas through a wash bottle containing a solution of caustic soda.

Examine the properties of the gas obtained.

III. To another 50 c.c. of the mixture add 200–300 c.c. of water, and distil, until about 50 c.c. have collected in the receiver. Add quick lime, in small lumps, to the distillate, avoiding much rise of temperature, and allow to stand for some hours. Re-distil, and carefully examine the distillate.

IV. Arrange an apparatus as shown in the accompanying photograph : the distilling flask is fitted with a thermometer, and
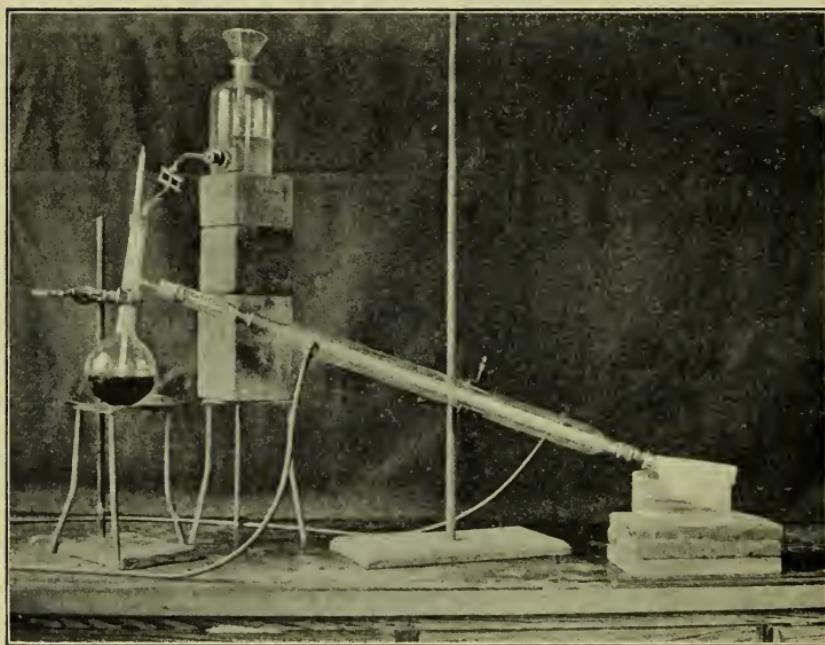
FIG. 10.

connected by a rubber tube with an aspirator containing alcohol : the tube is provided with a screw clamp.

Transfer the remainder of the mixture of acid and alcohol into the distilling flask, add 10 c.c. of alcohol, and heat until the thermometer, the bulb of which is immersed in the liquid, shows a temperature of 140°–145° C. Then by turning the screw clamp, allow alcohol to flow into the flask at such a rate that the temperature does not rise above 145° C., nor fall below 140° C. Ether will be given off continuously, and condense and collect in the

receiver, which should be well cooled. The stronger the heating, the more rapid must be the delivery of the alcohol; the condition essential for the success of the experiment is the maintenance of a constant temperature between 140° and 145° C. To remove the alcohol, wash the crude ether with saturated aqueous solution of common salt, in which the ether is only slightly soluble, and by means of a separating funnel, remove the lower layer. Then shake up in the same funnel with a dilute solution of caustic soda, which will remove any sulphur dioxide; again withdraw the lower layer of liquid, wash once more with salt solution, and separate. Pour the ether through the top of the funnel into a flask of suitable capacity, add some lumps of fused calcium chloride, and allow to stand for some hours. Finally, re-distil the ether over the water bath in the usual manner, collecting in a receiver the liquid which comes over between 33° and 37° C.

Investigate the properties of the ether obtained.

PREPARATION OF OXALIC ACID FROM SUGAR.

Weigh out 50 grams of powdered cane sugar, and place it in a beaker. Add 500 c.c. of nitric acid (sp. gr., 1·25), and gently heat : a brisk action takes place, which should be allowed to continue without any further heating until the evolution of brown fumes has ceased. The solution is then evaporated to about 100 c.c., and allowed to cool. The oxalic acid crystallises out, and is washed with several successive small quantities of cold water. More oxalic acid can be obtained by further concentration of the mother liquor, to which the washings should be added.

Oxalic acid, $\begin{matrix} COOH \\ | \\ COOH \end{matrix} \cdot 2H_2O$, crystallises in thin monoclinic
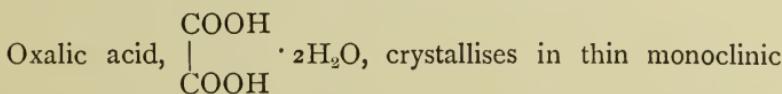
plates. It is a dibasic acid. It dissolves in water to the extent of about 10 in 100.

Exercise.—Estimate the water of crystallisation in the specimen of oxalic acid you have prepared by the method of oxidation with potassium permanganate (see p. 60).

PREPARATION OF THE THREE OXALATES
OF POTASSIUM.

Prepare a cold saturated solution of oxalic acid and add it, by means of a burette, to 50 c.c. of a solution of caustic potash, containing about 20 grams per 100 c.c., till exact neutrality has been reached—use phenolphthalein as indicator. Crystallise out the neutral potassium oxalate, by evaporating if necessary.

To the same quantity of the same potash solution add twice as much of the solution of oxalic acid as was used in the first experiment, and crystallise out the potassium acid oxalate.

Repeat the experiment, using the same quantity of potash solution and four times the amount of oxalic acid used in the preparation of the neutral oxalate, and crystallise the potassium quadroxalate.

Potassium oxalate, $\begin{array}{c} COOK \\ | \\ COOK \end{array} \cdot H_2O$, crystallises in monoclinic prisms. Solubility about 33 in 100 at ordinary temperature.

Potassium acid oxalate ("Salt of Sorrel"), $\begin{array}{c} COOK \\ | \\ COOH \end{array}$, occurs in monoclinic prisms of a different habit to that of the normal potassium salt. Solubility: $2\frac{1}{2}$ in 100 of water at 15° C., and 16·7 in 100 at 100° C.

Potassium quadroxalate, $\begin{array}{cc} COOK & COOH \\ | & | \\ COOH & COOH \end{array} \cdot 2H_2O$, crystallises in triclinic prisms. Solubility: 5 in 100 of water at 20° C.

PREPARATION OF THE TARTRATES OF SODA AND
POTASH.

Into two beakers place equal quantities of the same solution of caustic potash (20 per cent.). Exactly neutralise one portion with a solution of tartaric acid, about 20 per cent., and note carefully the amount used. To the second portion add double the volume

of the tartaric acid solution; a heavy crystalline precipitate of acid potassium tartrate (cream of tartar) will be produced. Filter, wash with cold water, and dry on a porous tile. The solution containing the neutral tartrate may be crystallised by evaporating the solution and cooling.

Repeat the experiments with caustic soda instead of caustic potash, and compare the salts obtained with the corresponding products of the first experiment.

Potassium tartrate, $COOK . CHOH . CHOH . COOK$, crystallises in rhombic prisms. It is very soluble in water.

Cream of Tartar, $COOK . CHOH . CHOH . COOH$, occurs in very small rhombic crystals. It is fairly soluble in boiling water.

Sodium tartrate, $COONa . CHOH . CHOH . COONa . 2H_2O$, and

Sodium acid tartrate, $COONa . CHOH . CHOH . COOH$-$H_2O$, crystallises more easily than potassium tartrate.

Note.—If the solutions of the tartrates become concentrated, syrupy liquids are formed which only crystallise after prolonged standing.

PREPARATION OF CALCIUM ACETATE AND ACETONE.

Into a large evaporating basin put 150 c.c. of glacial acetic acid diluted with twice its volume of water. Add precipitated chalk in small quantities at a time (stirring after each addition) until no effervescence occurs on adding the chalk. Filter, evaporate the filtrate to dryness on the water bath, and dry the solid calcium acetate so obtained in an air oven at 110° C.

Place 50 grams of the calcium acetate in a retort capable of holding about a quarter of a litre. Connect the retort to a condenser by means of an adapter, and heat carefully as long as vapours of acetone are evolved. Collect the acetone in a dry receiver, and purify by redistillation.

Acetone, $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CO$, is a pale yellow liquid which mixes in all proportions with water, alcohol, or ether. B.pt., 56·3° C. It is highly inflammable.

PREPARATION OF SOAP AND FATTY ACIDS FROM OLIVE OIL.

Prepare a solution of 20 grams of caustic soda in 20 c,c. of water, add 20 c.c. of methylated spirit, and place in an evaporating basin of about 100 c.c. capacity. Add slowly (and with stirring) 20 c.c. of olive oil. Evaporate on a water bath with constant stirring until a pasty residue remains. Dissolve the soap obtained in hot water, avoiding the formation of much lather : filter if necessary. Saturate the solution with common salt, allow to stand for a while, filter off the soap, and wash several times with small quantities of cold water. Examine the properties of the substance obtained.

Take about half the material from the above experiment, dissolve in hot water, and add hydrochloric acid as long as a precipitate is produced. Filter off the oily layer whilst still hot, using a filter paper which has been previously soaked in hot water, and wash well with boiling water, until the washings are free from acid, as shown by litmus paper. Allow to cool, and remove the cake from the filter paper.

Determine the melting point of the fatty acid, and demonstrate its acid nature by dissolving in alcohol and testing with damp litmus paper.

PREPARATION OF ESTERS.

Example : ETHYL ACETATE.

Use the apparatus described in the method given for the preparation of ether. Into the distilling flask place a mixture of 50 c.c. of concentrated sulphuric acid, and 50 c.c. of absolute alcohol, made by slowly adding the acid to the alcohol. In the aspirator, place a mixture of glacial acetic acid and absolute alcohol in equal volumes. Raise the temperature of the contents of the flask to 140° C., and then allow the mixture of acetic acid and alcohol to flow into the flask at such a rate that the temperature remains constant. Ethyl acetate will distil over

and collect in the receiver. Purify in the same manner as for ether.

Ethyl acetate, $CH_3COOC_2H_5$, is a colourless mobile liquid of a pleasant fruity smell. B.pt., $78°$ C.; sp. gr., o·9.

Exercise.—(1) Prepare amyl acetate or ethyl butyrate in a similar manner.

(2) Boil 20 c.c. of ethyl acetate with 40 c.c. of caustic potash solution (containing 35 grams per 100 c.c.) for half an hour in a flask fitted with a reflux condenser. Then distil the liquid in the ordinary way, and collect the first 10 c.c. which come over. What is the distillate ?

PREPARATION OF SILICON TETRAFLUORIDE.

Mix finely powdered fluorspar with about its own weight of

FIG. 11.
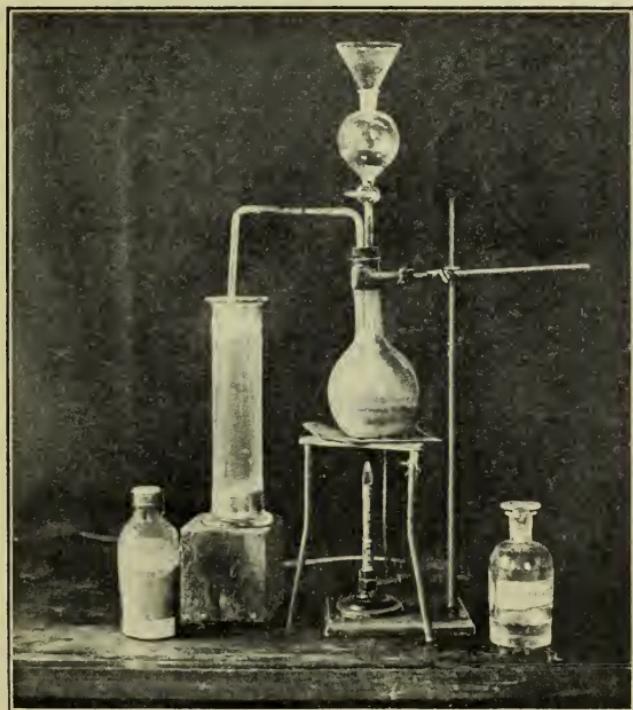
dry sand. Place it in a flask of suitable size fitted with a safety funnel and delivery tube. Add concentrated sulphuric acid, and

gently warm. Silicon tetrafluoride is evolved as a colourless gas, which may be collected in a perfectly dry gas cylinder by downward displacement; or, instead of this, the delivery tube may be made to dip just under a layer of mercury at the bottom of a gas jar which is filled with water. On passing the gas through the mercury into the water, it is immediately decomposed, with formation of a gelatinous precipitate of hydrated silica, and of fluosilicic acid, which remains in solution.

In performing this experiment, it is necessary to prevent any water from entering the delivery tube, as the deposit of silica formed would choke the exit. This is secured by the use of the layer of mercury.

The solution of fluosilicic acid may be neutralised with potassium carbonate or hydroxide, and the resulting potassium fluosilicate obtained as a crystalline precipitate.

PREPARATION OF LEAD DIOXIDE.

(First Method.)

Dissolve about 20 grams of lead nitrate in water with the addition of a little nitric acid to clear the solution, and put it into a large evaporating basin. Prepare also a solution of bleaching powder in *cold* water and filter it.

To the solution of lead nitrate add caustic soda in slight excess, or as long as a precipitate is produced, and warm. Then add the clear solution of bleaching powder. The white precipitate of lead hydroxide will rapidly turn brown, and the bleaching powder solution must be added until no further darkening takes place. The mixture must be kept hot during the entire process. Allow to settle, decant off the clear liquid, and wash the residue by decantation, first with dilute nitric acid, and then with water. Drain the brown lead dioxide, and dry in a steam oven.

What is the action of the bleaching powder solution?

(Second Method.)

Weigh out carefully 10 grams of red lead, and place it in an evaporating basin or beaker. Add nitric acid of 1·2 sp. gr.

in sufficient quantity to completely decompose the red lead, and to remove all traces of red colour. Heat gently, and filter hot; wash the precipitate thoroughly with hot water, and collect the washings along with the filtrate. Dry the lead dioxide at a temperature not exceeding 100° C. and weigh; the weight of the dried filter paper should have been previously ascertained. Evaporate the filtrate to dryness on the water bath, finish drying in the steam oven, and weigh the residue in the evaporating basin, which must also have been previously weighed. From the results obtained, deduce an equation representing the action of nitric acid on red lead.

Lead dioxide, PbO_2, is a dark purple-brown amorphous powder, insoluble in water and nitric acid; it is decomposed by hydrochloric and sulphuric acids, yielding the corresponding salts of the lower oxide.

Exercise.—Examine quantitatively the action of heat upon lead dioxide.

PREPARATION OF LEAD CHROMATES.

Dissolve 5 grams of lead acetate in distilled water, with the addition of a drop or two of acetic acid, and filter, if necessary. Add a solution of potassium dichromate until the liquid above the precipitate is *slightly* yellow. Filter, wash thoroughly, and dry in a steam oven. The precipitate obtained is normal chromate of lead ($PbCrO_4$), and is used as a pigment under the name of chrome yellow.

Repeat the experiment with the same quantities of materials, but wash the precipitate by decantation, and add a dilute solution of caustic soda, and boil. The precipitate will partially dissolve, and the remainder is converted into basic chromate of lead ($PbCrO_4$. PbO), a solid of a deep orange-red colour, also used as a pigment under the name of chrome red. Wash and dry in the usual way.

Mixtures of these two precipitates form the various shades of chrome orange.

PREPARATION OF BASIC LEAD NITRATE.

Finely powder 20 grams of lead nitrate, and dissolve in 150 c.c. of water. Separate into two portions of 70 and 80 c.c. respectively, and add to the larger quantity a slight excess of ammonia. The white precipitate produced is lead hydroxide. Allow to settle, and wash several times with hot water by decantation. Add the washed precipitate to the remaining portion of the solution of lead nitrate previously diluted to half a litre, and boil for at least 15 minutes, keeping the bulk of the solution constant by the addition of water as required. Filter while hot, and wash the residue several times with hot water, adding the washings to the filtrate. Evaporate the filtrate to a small volume, not much exceeding 50 c.c. and allow to cool. Recrystallise the product from hot water. Dry the crystals on a porous tile.

Basic lead nitrate, $Pb(OH)_2 . Pb(NO_3)_2$, crystallises in brilliant scales which are only slightly soluble in cold water.

PREPARATION OF STANNIC CHLORIDE.

Fit a test-tube 8 inches long and $1\frac{1}{4}$ inch in diameter with a cork bored with two holes. Through one of these insert a long straight tube about three feet in length, to act as an air condenser; through the other hole in the cork, the delivery tube from a chlorine apparatus should pass loosely, so that the position of the tube may be varied as required. Fill the test-tube with granulated tin, and place the apparatus in a vertical position, supporting it by means of a clamp. Pass in a slow current of dry chlorine; liquid tin tetrachloride will be formed, and the delivery tube should be moved from time to time so as to keep the end dipping just below the surface of the liquid. When the action is completed, pour off the liquid from any residual tin into a small distilling flask, and purify by fractional distillation, collecting the portion which comes over between 110° and 118° C. Preserve in a sealed tube.

Stannic chloride, $SnCl_4$, is a colourless liquid which gives thick white fumes in the air. B.pt., 114° C. It solidifies at $-33°$ C. to
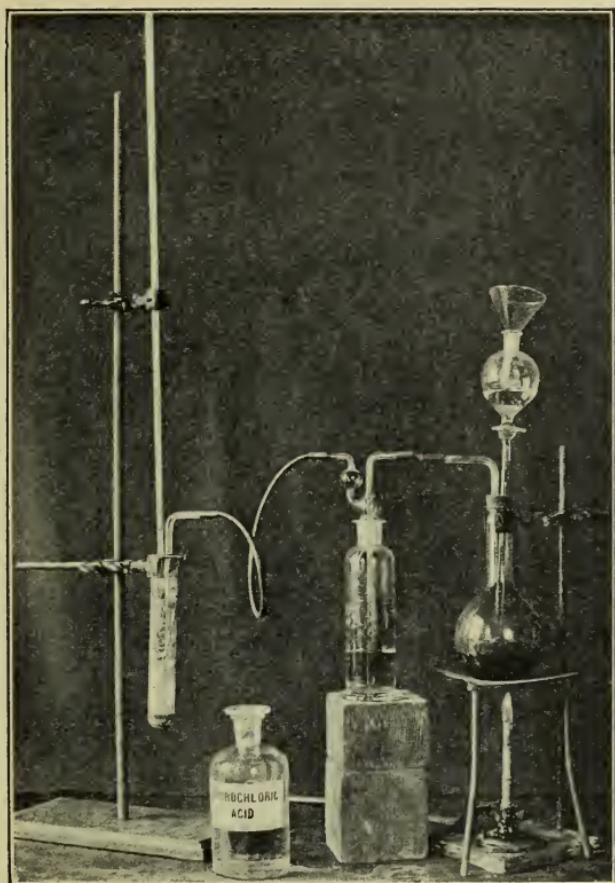
FIG. 12.

small white crystals; sp. gr., 2·23. It combines with water to form crystalline hydrates.

PREPARATION OF BORIC ACID.

Dissolve 40 grams of borax in 100 c.c. of boiling water, and add 25 c.c. of concentrated hydrochloric acid, maintaining the temperature near the boiling point of the solution. Allow to cool

slowly, collect the crystals upon a filter paper in a Buchner funnel, wash with small quantities of cold water till free from chloride. Drain as far as possible on the funnel ; complete the drying upon a porous tile.

The substance obtained should consist of colourless scaly crystals with a pearly lustre and soapy feel. It is ortho-boric acid, H_3BO_3. Solubility : 4 in 100 of water at 20° C., and 34 in 100 at 100° C. It is soluble in alcohol.

Exercise.—Moisten a piece of turmeric paper with a solution of boric acid—note the colour-change ; then touch the discoloured portion with a glass rod dipped in caustic soda solution, and compare the effect with that of alkalis alone on turmeric paper.

PREPARATION OF BORON TRIOXIDE.

Weigh out $12\frac{1}{2}$ grams of boric acid, place in a crucible, and heat carefully over a Bunsen burner, gradually raising the temperature to a red heat, until the weight is constant. The residue is boron trioxide, a glassy mass which is usually somewhat discoloured.

Note.—Ortho-boric acid may be heated to 70° C. without loss of water ; at 100° C. it is converted into metaboric acid, HBO_2, and at 160° C. pyroboric acid, $H_2B_4O_7$, is obtained.

PREPARATION OF AMMONIUM ALUM.

Dissolve separately in small quantities of water 10 grams of aluminium sulphate and 2 grams of ammonium sulphate ; filter if necessary, and mix the solutions. Allow to crystallise at the ordinary temperature.

The substance crystallises extremely well, and an attempt should be made to grow a crystal of good shape, by suspending in the solution, by means of a hair or very fine thread, one of the best crystals first formed.

A crystal of iron alum and of chrome alum should also be obtained in the same way.

Ammonium alum, $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$, crystallises in

octahedra belonging to the cubic system. It is isomorphous with
the other "alums."

Exercise.—Prepare in a similar way crystals of potassium
magnesium sulphate, $K_2SO_4 . MgSO_4 . 6H_2O$; ammonium zinc sul-
phate, $(NH_4)_2SO_4 . ZnSO_4 . 6H_2O$; potassium manganese sulphate,
$K_2SO_4 . MnSO_4 . 6H_2O$. These are not alums, but are comparable
with ammonium ferrous sulphate (see p. 6).

PREPARATION OF ALUMINIUM CHLORIDE.

Fit up an apparatus for the preparation of hydrochloric acid
gas. A Kipp will be found the most convenient for this purpose,
and the gas is best prepared by the action of concentrated sul-
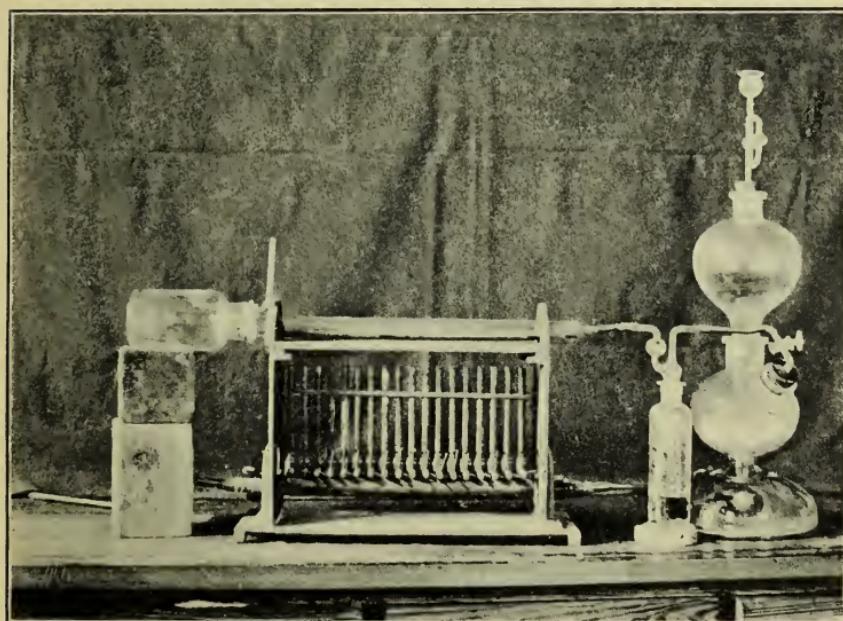
FIG. 13.

phuric acid on fused ammonium chloride. The delivery tube
from the apparatus must be connected with a wash bottle of fair
size, containing concentrated sulphuric acid for thoroughly drying
the gas ; the exit tube from the wash bottle passes through
a cork in one end of a piece of hard glass tubing 30 cm. long,

and not less than 2 cm. in diameter. The other end of the hard glass tube must pass through a large cork fitted into a very wide-necked bottle. A second glass tube of narrower diameter and considerable length, bent once at right angles, is also passed through the cork, for the purpose of carrying off the hydrogen which is liberated during the reaction. The cork and exit tube may advantageously be protected from the heat of the furnace by a small screen of asbestos.

Introduce into the hard glass tube pieces of aluminium foil, in sufficient quantity to form a layer reaching along the greater part of the length of the tube to a depth of about half its dia-meter. Plugs of loosely packed asbestos should be inserted near each end of the tube to keep the aluminium in position, **but they must be in the part of the tube which is heated by the furnace.** The hard glass tube is then placed on a furnace of such a length that only 2–3 cms. of the tube project beyond the furnace, and a **very** rapid current of hydrochloric acid passed over the metal ; as soon as, **but not before,** all the air is expelled from the apparatus, the aluminium is heated throughout its entire length, at first with small flames ; it may afterwards be heated more strongly, but **the temperature must not be allowed to become high enough to melt the metal.**

The aluminium chloride will be carried over into the receiver, and will condense as a white solid. It is obvious that the whole apparatus must be perfectly dry.

Aluminium chloride, $AlCl_3$, is a white solid, vaporising with-out fusion at 183° C. It evolves fumes of hydrochloric acid on exposure to moist air, and for this reason must be kept in closely stoppered bottles.

PREPARATION OF MAGNESIUM SULPHATE FROM DOLOMITE.

Add 15 grams of finely powdered dolomite in small instal-ments to 150 c.c. of 2**N** sulphuric acid contained in a beaker of about a quarter of a litre capacity. Heat for a short time

to complete the decomposition of the dolomite; allow to cool and filter: the solution contains the sulphate of magnesium and a small quantity of calcium sulphate. Separate by re-crystallising two or three times.

Magnesium sulphate, or Epsom Salts, $MgSO_4 . 7H_2O$, occurs in colourless needle-shaped rhombic prisms. Solubility: 36·2 in 100 of water at 20° C.; 73·8 in 100 at 100° C.

COMPARISON OF THE ACTION OF POTASSIUM DICHRO-MATE ON MERCUROUS NITRATE AND MERCURIC CHLORIDE.

(1) To a solution of mercurous nitrate, cleared if necessary by the addition of a few drops of dilute nitric acid, add a fairly concentrated solution of potassium dichromate as long as a precipitate is produced. Filter, wash, and dry.

The precipitate is mercurous chromate; study the action of heat upon this salt, and note the evolution of the oxygen, sublimation of mercury, and the residue of chromium sesquioxide.

Mercurous chromate, Hg_2CrO_4, is a red amorphous powder, insoluble in water.

(2) Dissolve molecular proportions of mercuric chloride and potassium dichromate in separate quantities of hot water; mix the solutions and allow to stand. A highly crystalline orange-red precipitate is deposited, which consists of the double salt, $K_2Cr_2O_7 . HgCl_2$. Examine the action of heat on this substance.

(3) Add to a solution of neutral potassium chromate a solution of mercuric chloride. Collect and wash the precipitate produced; it is mercuric chromate, $HgCrO_4$. As it is very soluble in excess of mercuric chloride, care must be taken that this salt is not added in excess.

PREPARATION OF PURE SODIUM CHLORIDE.

Make a concentrated solution of common salt; half a litre will be a convenient quantity. Place the solution in a fairly wide beaker, and pass in dry hydrochloric acid gas [1] through an inverted funnel dipping just below the surface of the liquid. Sodium chloride, being only slightly soluble in concentrated hydrochloric acid, is precipitated as the solution becomes saturated with the
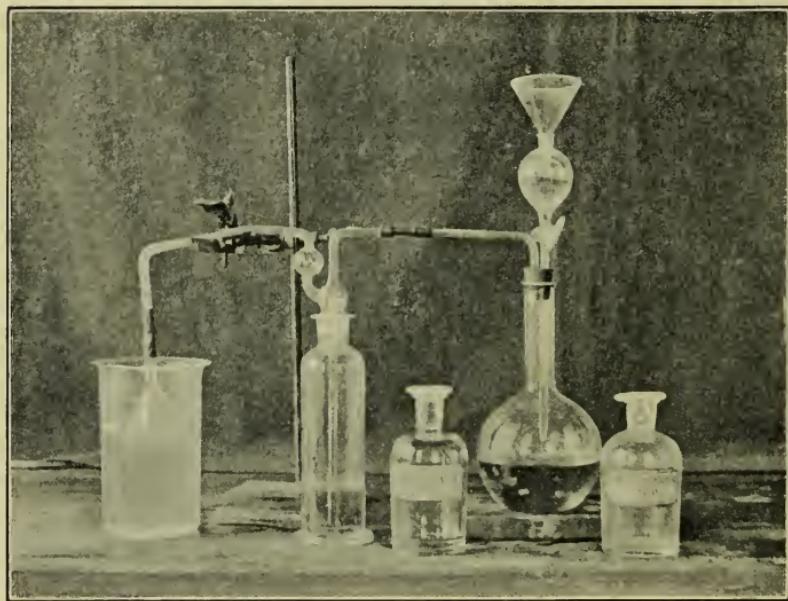
Fig. 14.

gas. Filter, wash with pure concentrated hydrochloric acid, remove from the filter paper, dry on a porous tile, and finally heat strongly in an evaporating basin to expel the last traces of hydrochloric acid.

Sodium chloride, NaCl, crystallises in small cubes. Solubility: $35 \cdot 75$ in 100 of water at $15°$ C., and $39 \cdot 6$ in 100 at $100°$ C.

[1] This is most conveniently obtained by allowing concentrated sulphuric acid to drop into concentrated hydrochloric acid, and drying the gas by passing it through a wash bottle containing concentrated sulphuric acid (see figure).

It is not soluble in alcohol. M.pt., about 790° C.; it begins to volatilise at that temperature.

PREPARATION OF AMMONIA COPPER SULPHATE.

This compound is the cause of the blue colour obtained by adding excess of ammonia to copper sulphate solution—similar compounds may be obtained with other copper salts.

Prepare a solution of copper sulphate by dissolving 10 grams of the salt in 50 c.c. of water, and add concentrated ammonia until the precipitate which is first formed is redissolved. On to the top of the liquid (which should be quite cold), a deep layer of alcohol is poured by means of a pipette, and the liquids allowed to mix by diffusion. If the experiment has been properly conducted, after some weeks' standing long deep blue transparent crystals will be obtained, which must be drained rapidly, dried on a tile, and sealed up in a glass tube with as little exposure to the air as possible, since they lose ammonia in the open air.

The compound has the formula $CuSO_4 . 4NH_3 . H_2O$; four molecules of water of crystallisation have been replaced by ammonia.

PREPARATION OF THE DOUBLE SULPHATE OF COPPER AND AMMONIUM.

This salt can be obtained by crystallising together the sulphates of copper and ammonium in molecular proportions, in a similar manner to ferrous ammonium sulphate. It has the formula $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$, and occurs in monoclinic crystals. Solubility : 66·7 in 100 of water at 100° C.; less soluble in cold water. It effloresces in dry air.

PREPARATION OF CUPROUS CHLORIDE.

(1) Dissolve 10 grams of cupric chloride in 50 c.c. of water, with the addition of 10 c.c. of concentrated hydrochloric acid, and pass into the solution sulphur dioxide until the green colour of the liquid has completely disappeared.

The cuprous chloride, being very slightly soluble in water or very dilute hydrochloric acid, separates from the liquid in small white crystals, which must be filtered off, drained, and dried on a tile as rapidly as possible. It is then advisable to seal them up in a glass tube, as they oxidise and turn green on exposure to air.

(2) Dissolve 20 grams of basic copper carbonate in 200 c.c. of concentrated hydrochloric acid in a flask. Add excess of clean copper turnings, and boil until a nearly colourless solution is obtained. The solution now contains cuprous chloride, which is soluble in concentrated hydrochloric acid; pour it into a large quantity of cold water. The cuprous chloride will be precipitated as a snow-white powder, amorphous or obscurely crystalline. The precipitate should be washed with cold boiled water several times by decantation, drained, and dried rapidly on a tile. The cuprous chloride in this amorphous form oxidises even more readily than the crystalline variety.

PREPARATION OF CUPROUS OXIDE.

(1) Prepare cuprous chloride according to the first method given, but instead of separating off the crystals, add an excess of a concentrated solution of sodium carbonate, and boil. A dull yellow precipitate of cuprous oxide is deposited; filter, wash with water, alcohol, ether, in succession, and dry in the air.

(2) Twelve grams of copper sulphate are dissolved in 50 c.c. of water, and 60 grams of Rochelle salt dissolved in 150 c.c. of water. The two solutions are mixed, and to the mixture is added a solution of 25 grams of caustic soda in 50 c.c. of water. A clear deep blue solution is so obtained.

The liquid is heated nearly to the boiling point, and *small* quantities of a dilute solution of grape-sugar (glucose) are added, the solution being boiled for a minute or two after each addition. The total amount of grape-sugar used must be only just sufficient to remove the blue colour of the solution. The cuprous oxide settles down as a bright red powder, which should be filtered off

through glass wool, washed with water, alcohol, and ether, and air-dried, as before.

Cuprous oxide, Cu_2O, is a red, orange, or yellow amorphous powder; its colour varies with the method of preparation.

Note.—In order to obtain a good coloured specimen, care must be taken to avoid the addition of more grape sugar than is necessary to reduce the cupric oxide.

Exercise.—Examine the action of acids upon cuprous oxide.

VOLUMETRIC ANALYSIS

Whilst ultimately all question of the composition of a substance is referred to mass, analyses which depend on direct weighing are usually long and tedious. The "volumetric" processes, however, provide methods which are extensively used, as they are invariably quicker, and a fairly correct result is easily obtained.

The principle underlying these volumetric processes is that of using "standard" solutions of some reagent which has a sharp and definite chemical action with the substance to be estimated. The solutions are "standard" in that they contain a known mass of the selected reagent in a given volume, or are made so that a known volume exactly reacts with a definite mass of the substance to be estimated.

Whilst it is immaterial, as far as the principle is concerned, exactly what may be the concentration of these "standard" solutions, yet it is convenient to adopt a uniform method of denoting the content of such solutions, if only to enable one to express one's working in such terms as to be intelligible to others.

The method in general use is that of the **normal** solution, which is thus defined :—

A **normal** solution is one which contains **one gram-equivalent** (the equivalent weight in grams) of the **active substance** in one litre.

The equivalent weight of any substance depends upon the reaction in which it is taking part.

Fundamentally, the equivalent weight is defined as the mass of the substance which reacts with, or liberates, 1 gram of hydrogen,

or 8 grams of oxygen, but the reaction may involve neither of these elements directly. The chief point for the student to consider is the actual reaction with which he has to deal. In the case of neutralisation of acids and alkalis, the **equivalent** of an acid is clearly that mass which yields 1 gram of replaceable hydrogen, while the equivalent for a base is similarly that mass which replaces one gram of hydrogen in the acid by a metal.

For example—
$$HCl + KOH = KCl + H_2O$$
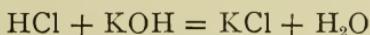
evidently one gram-molecule (molecular weight in grams) of hydrochloric acid yields 1 gram of hydrogen, whilst one gram-molecule of caustic potash replaces one gram of hydrogen by potassium, at the same time forming water.

The equivalent, then, of hydrochloric acid is 36·5, that of potassium hydroxide 56.

Again—
$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O$$
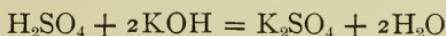
there one gram-molecule of sulphuric acid yields 2 grams of hydrogen, and its equivalent is therefore $\frac{98}{2} = 49$.

Similarly barium hydroxide reacts with 2 hydrogen atoms per molecule—
$$2HCl + Ba(OH)_2 = BaCl_2 + 2H_2O$$
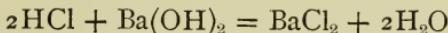
and its equivalent is therefore half its molecular weight in grams, *i.e.* for the crystallised $Ba(OH)_2 . 8H_2O$, the equivalent is $\frac{315}{2} = 157·5$.

Two cases where the equivalent of a substance is different according to the reaction may be briefly mentioned.

(1) The equivalent of iron when a ferrous salt is oxidised to the ferric compound is, as is shown later (p. 57), 56, whilst the equivalent in the reaction
$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$
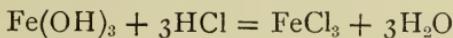
is clearly $\frac{56}{3} = 18·67$,
and in the reactions
$$FeS + 2HCl = FeCl_2 + H_2S$$
and
$$Fe + 2HCl = FeCl_2 + H_2$$
it is $\frac{56}{2} = 28$.

(2) The equivalent of nitric acid in neutralising a base is 63—

$$HNO_3 + KOH = KNO_3 + H_2O$$
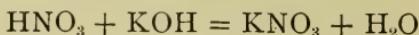
but as an oxidising agent it is different. These oxidising actions of nitric acid are obscure and probably far from simple, but one may suppose that nitric acid in certain circumstances acts with nascent hydrogen thus

$$2HNO_3 + 6H = 4H_2O + 2NO.$$
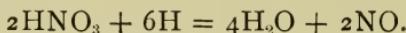
Here the equivalent is $\frac{1}{3}HNO_3 = 21$.

A more complicated case is afforded by potassium permanganate. Here the "active substance" is not really the permanganate, but the oxygen which it gives up. Further, it is only a part of the oxygen of the permanganate which is used in oxidation.

To find the "equivalent" of the permanganate, it is necessary to know how it breaks up. This is shown by the equation

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$
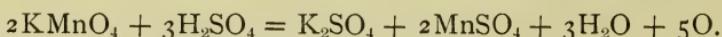
In other words, 316 grams of potassium permanganate will give 5×16 grams = 80 grams of oxygen. (The oxygen is not set free as such, but is used in the oxidation process.) The equivalent of potassium permanganate is therefore $\frac{316}{10} = 31\cdot6$.

It often happens that a "normal" solution is either more concentrated, or less, than is desirable for the particular estimation to be made. One then uses solutions which are submultiples or multiples of a "normal" solution, as the case may be. As a matter of fact, the submultiple strengths are the more frequently used; the submultiple is indicated by the Latin prefix as in subdivisions of the metre. A solution of a concentration one-tenth that of a normal solution is thus called a "decinormal" solution.

Multiple strengths may be denoted by the Greek prefix, again on analogy with the Metric System of length-measurement; though the English multiple-numerals twice, ten times, and so on, are often used. The solutions are, however, not employed to any great extent in ordinary simple volumetric analyses.

The term "normal" is conveniently abbreviated to the

symbol **N**, so that a normal solution of any substance is denoted by a capital **N** preceding its chemical formula; thus a normal solution of caustic potash is expressed **N** . KOH. Similarly, a decinormal solution of potassium dichromate would be represented as $\frac{N}{10}$ $K_2Cr_2O_7$. Such a solution contains 4·9 grams of potassium dichromate per litre.[1]

The phrase " molecular solution " is sometimes employed to indicate a solution containing one gram-molecule (molecular weight in grams) per litre, and this must be carefully distinguished from the " normal solution." One may illustrate by the example of potassium permanganate.

The molecular weight of potassium permanganate is 158, and a molecular solution, **M** . $KMnO_4$, contains 158 grams per litre. A decimolecular solution, $\frac{M}{10}$ $KMnO_4$, contains 15·8 grams per litre.

A normal solution contains, as we have seen above, 31·6 grams per litre, that is, a **deci**-molecular and a **semi**-normal solution are of the same concentration.

So a decinormal solution of potassium permanganate contains 3·16 grams per litre, and is a $\frac{1}{50}$ molecular solution.

ESTIMATION OF ACIDS AND ALKALIS.

The chief standards used here are solutions of sodium carbonate, sulphuric acid, hydrochloric acid, caustic soda, and caustic potash.

As it is difficult to obtain all except the first of these substances in a pure condition, it is customary to make sodium carbonate the starting point, and to standardise the others by means of it.

The preparation of perfectly pure anhydrous sodium carbonate is, as will be seen, usually a long and tedious process; whilst it is probably the best for very accurate work, the authors have found

[1] The student should satisfy himself that he understands why this is so.

that a very convenient basis for ordinary work is afforded by commercial pure citric acid crystals, which can usually be obtained sufficiently pure from the dealers, and made up into the starting standard solution without any further process of purification. By the use of this standard, caustic soda can be prepared, thence the mineral acids, and finally sodium carbonate if required.

PREPARATION OF DECINORMAL CITRIC ACID SOLUTION.

Citric acid has the formula $C_3H_4(OH)(COOH)_3 + H_2O$, and is a tribasic acid, that is, it gives three hydrogen atoms per molecule or 3 grams hydrogen per gram-molecule on neutralisation with caustic soda. Its equivalent is therefore 70, and a decinormal solution will contain 7 grams per litre.

Accordingly 7 grams of pure crystallised citric acid should be accurately weighed out, and dissolved in about 300 c.c. of hot water. After cooling, the solution is made up to 1000 c.c. and thoroughly mixed.

PREPARATION OF DECINORMAL CAUSTIC SODA.

In the preparation of caustic soda standard solutions, one must start with a known solution of acid. One may conveniently use the $\frac{N}{10}$ citric acid solution prepared as above.

About 6 grams of ordinary pure caustic soda should be dissolved in about 1200 c.c. of water, and the solution well mixed. 10 c.c. of this solution should be placed in a small flask (about 100 c.c. capacity), and one drop of a dilute alcoholic solution of phenolphthalein added.

A burette, which has been carefully cleaned and washed out with the standard solution, is then filled with the $\frac{N}{10}$ citric acid, and the level brought exactly to the zero mark. It will be found best to take the bottom of the meniscus in all cases as the level of the surface; this will be brought out most distinctly by the

use of a white background. (Care should be taken that no air-bubble is left in the burette, nor in the narrow jet below the tap or clip.) Burettes can be bought which are provided with opaque white glass at the back, but an ordinary burette can be made quite as effective by painting the back (on the outside) with white enamel such as is used for painting golf balls. If it is preferred to keep the glass clear, the level of the meniscus can be read by holding a piece of white paper behind the burette.

Having filled the burette and adjusted the level to **0 c.c.**, the acid is now gradually run into the alkali, which is coloured pink by the phenolphthalein, until the colour just disappears; the solution in the flask should be kept thoroughly mixed by gentle but continuous agitation. The level of the meniscus is read, and the volume of acid added entered in the note-book.

The experiment is repeated several times; until, in fact, three successive readings are fairly concordant. The mean of these three readings is taken as the true one. The strength of the alkali can now be very simply calculated.

It is important to note at the outset, that the calculation can be much simplified if one bears in mind the fact that a decinormal solution of any substance is equivalent to a decinormal solution of any other, regard being given to the meanings of the terms " normal solution " and " equivalent." The " equivalent " will depend on the nature of the reaction which is under investigation (see p. 44).

So in this case—

1 c.c. of $\dfrac{N}{10}$ citric acid will neutralise 1 c.c. $\dfrac{N}{10}$ NaOH.

,,   ,,   ,,   0·004 gram NaOH

and one does not need to take the weight of citric acid used into consideration, once one has prepared the $\dfrac{N}{10}$ citric acid solution.

Suppose, for example, 12·3 c.c. of acid had been used; this would have neutralised 12·3 c.c. $\dfrac{N}{10}$ NaOH. Hence 10 c.c. of the caustic soda solution contain as much alkali as 12·3 c.c. $\dfrac{N}{10}$ NaOH.

E

To make the soda solution decinormal, all that is necessary, then, is to dilute every 10 c.c. to 12·3 c.c. The solution can therefore be made decinormal either by taking 1000 c.c., and adding to that 230 c.c. of water, or by placing $\frac{10 \times 1000}{12\cdot3} = 813\cdot00$ c.c. in a litre flask, and adding water up to the 1000 c.c. mark. The former is perhaps the simpler way ; it involves the assumption, which in the case of more concentrated solutions may not be justified, that the volume after dilution is the sum of the volume of the solution and the volume of the water added. The $\frac{\mathbf{N}}{10}$ NaOH is, after thoroughly mixing, ready for use.

The correctness of its concentration should be confirmed by titrating with the $\frac{\mathbf{N}}{10}$ citric acid. The volume of $\frac{\mathbf{N}}{10}$ acid should be exactly that of the caustic soda taken. If this is not the case, a fresh start may be made, or the solution may be diluted or strengthened, or a factor may be used (*e.g.* 1 c.c. = 0·996 c.c. $\frac{\mathbf{N}}{10}$ NaOH). The second course is usually not satisfactory, and the last increases the labour of arithmetic in calculations.

PREPARATION OF DECINORMAL HYDROCHLORIC ACID.

Fifteen c.c. of concentrated hydrochloric acid is diluted to 1100 c.c., the solution well mixed, and placed in a burette with the same precautions as above.

Ten c.c. of $\frac{\mathbf{N}}{10}$ NaOH are placed in a flask, a drop of phenolphthalein added, and the amount of acid required to neutralise this amount of $\frac{\mathbf{N}}{10}$ NaOH determined.

Suppose 8·7 c.c. were required. This means that 8·7 c.c. of the acid were equal to 10 c.c. $\frac{\mathbf{N}}{10}$ HCl, that is, every 8·7 c.c. must

be diluted to 10. So the acid can be made decinormal, either by taking 870 c.c. of acid and making up to 1000 c.c. in a flask, or by measuring 1000 c.c. and adding to it $\dfrac{130 \times 1000}{870} = 149\cdot4$ c.c. water.

The diluted solution is well mixed, and the correctness of its concentration confirmed by titration with the $\dfrac{N}{10}$ NaOH. Ten c.c. of the latter should now neutralise exactly 10 c.c. of the acid.

PREPARATION OF DECINORMAL SULPHURIC ACID.

This is made in the same manner as $\dfrac{N}{10}$ HCl, but only 4 c.c. of concentrated sulphuric acid are required for 1200 c.c.

PREPARATION OF DECINORMAL SODIUM CARBONATE.

About 7 grams of anhydrous sodium carbonate are dissolved in 1200 c.c. of water, and from this exactly $\dfrac{N}{10}$ Na_2CO_3 is obtained by titration with $\dfrac{N}{10}$ HCl or $\dfrac{N}{10}$ H_2SO_4, using methyl orange as indicator; procedure and calculation similar to above.

Exercises.—Having prepared some, or all, of these standard solutions, the student should now practise the operation of titration until he has acquired dexterity and confidence in the accuracy of his work. For this purpose, he should determine the concentrations of solutions selected from those suggested below, first merely expressing his results as fractions of normal solutions, and later giving the amounts by mass contained in a litre.

The titrations will be exactly similar in procedure to those described in the preparation of the standard solutions, with the exception that some thought may be necessary in selecting the

appropriate indicator in accordance with the considerations detailed under the head " Use of Indicators " on page 54.

Solutions suggested for practice.

ACIDS $\left(\frac{N}{5}, \frac{N}{10}, \frac{N}{20},\text{ and intermediate strengths}\right)$: sulphuric, hydrochloric, nitric, citric, oxalic, tartaric, acetic.

ALKALIS $\left(\frac{N}{5}, \frac{N}{10}, \frac{N}{20},\text{ and intermediate strengths}\right)$: caustic soda, caustic potash, lime in sugar solution, sodium carbonate, sodium bicarbonate, lithium carbonate, potassium bicarbonate, ammonia.

ALTERNATIVE METHOD FOR OBTAINING STANDARD SOLUTIONS OF ACIDS AND ALKALIS.

PREPARATION OF NORMAL SODIUM CARBONATE.

For the purposes of practice in the manipulation of volumetric analysis, one may use, without any further ado, ordinary pure anhydrous sodium carbonate as obtained from the shops, but it is often desirable, from an educational point of view, or in order to render the student able, should occasion arise, to be independent of any reliance on the purity of commercial substances, that the starting standard should be prepared in a state of purity by the student himself.

For this purpose, one starts with sodium bicarbonate. A little of the sample is dissolved in water, rendered strongly acid with nitric acid, boiled to expel carbon dioxide, and tested for chloride with silver nitrate, and, in another portion, for sulphate with barium nitrate. If either of these impurities is present, about 150 grams of the bicarbonate should be well stirred up in 100 c.c. of cold distilled water, filtered by the aid of the filter pump, well pressed and drained, and then washed with several successive quantities of water (about 20 c.c. each). The bicarbonate must be drained completely between each addition of water. After half a dozen washings, the last washing water is collected in a clean test-tube, and examined, as before, for sulphate and chloride. If either of these is still present, the

washing must be continued; usually, however, the treatment suggested above is sufficient to remove every trace of these impurities.

The sodium bicarbonate, after draining with the filter-pump as completely as possible, is now dried in the steam oven. About 100 grams of the bicarbonate should be heated in an open dish of platinum or porcelain[1] over an ordinary Bunsen burner with constant stirring for half an hour. The dish is then placed in a desiccator, allowed to cool completely, and weighed. The heating is repeated for a further period of ten minutes, and the dish again weighed after cooling in a desiccator. The process of ten minutes' heating is repeated until the weight remains constant.

Fifty-three grams of this pure sodium carbonate should then be quickly but accurately weighed out, dissolved in water, made up to 1000 c.c., and the solution well mixed.

PREPARATION OF DECINORMAL SODIUM CARBONATE.

Fifty c.c. of the $N . Na_2CO_3$ prepared above are placed in a 500 c.c. flask, and water added to the 500 c.c. mark, and the contents of the flask well mixed.

PREPARATION OF OTHER SOLUTIONS.

$\frac{N}{10}$ HCl, $\frac{N}{10}$ H$_2$SO$_4$ are now prepared as described in the method first given, only in this case they will be standardised from the $\frac{N}{10}$ Na$_2$CO$_3$, and methyl orange must be used as indicator.

$\frac{N}{10}$ NaOH can be prepared and standardised against the $\frac{N}{10}$ acid in a similar manner.

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[1] Porcelain is not good, as the carbonate attacks the glaze, and thus becomes impure. The amount, however, is usually not such as to introduce any noticeable error.

USE OF INDICATORS.

The three indicators most commonly used in working with acid and alkali solutions are phenolphthalein, methyl orange, and litmus. The student should accustom himself to the use of all three, but it is necessary that he should recognise at the earliest stage that they are not all equally suitable for every case.

Phenolphthalein is extremely sensitive to weak acids, but it is not sensitive to weak bases. In consequence, it is not a suitable indicator for use with ammonia; on the other hand, it is the only one of the three which gives reliable results with organic acids. In consequence of its being so easily affected by acids, it is not possible to estimate carbonates by acids with phenolphthalein as indicator as a general rule, unless the acid is run into the alkali and the solution be boiled after each addition. In this case the carbon dioxide is expelled from the solution, and the residue of the carbonate acts merely as a base. In the case of the alkalis, however, $NaHCO_3$ and $KHCO_3$ are neutral to phenolphthalein—a fact which is of practical importance, as will be seen later (p. 55).

Methyl orange is sensitive to weak bases, and is therefore always employed in ammonia estimations. It is, however, very unsatisfactory with feeble acids, and cannot be used for any organic acids. It is practically unaffected by carbon dioxide, and can therefore be used for the estimation of carbonates in the cold.

Supposing, however, that one wishes to use an organic acid with a carbonate solution, one is obliged to use phenolphthalein, and run the acid into the alkali (*not the reverse*); the alkali solution must be kept at the boiling point, and the solution well boiled before the final reading is taken.

The student may, very profitably, work out for himself the rationale of this process.

Litmus is more akin to phenolphthalein than to methyl orange, and can generally be used in the cases in which phenolphthalein is a suitable indicator.

Other things being equal, *i.e.* if any of the three indicators may be used, phenolphthalein or litmus is to be preferred to methyl orange. For the last named has the great drawback that the neutral point is difficult to perceive, especially in artificial light; it is well to remember that this difficulty is diminished by reducing the amount of indicator used to a minimum.

Exercises on the Use of Indicators.—(1) Titrate a solution of sodium carbonate with $\frac{N}{10}$ acid, using methyl orange, litmus, and phenolphthalein in turn as indicator, and performing the titration in the cold and at the boiling point.

(2) Investigate in a similar manner the behaviour of these indicators in the titration of ammonia by $\frac{N}{10}$ acid.

ESTIMATION OF SODIUM HYDRATE AND CARBONATE IN GIVEN SOLUTION.

The most simple method of carrying out this estimation depends on the fact that $NaHCO_3$ gives a neutral reaction to phenolphthalein whilst it is still alkaline to methyl orange.

If, then, one runs standard acid into a solution of caustic soda and sodium carbonate, in presence of phenolphthalein, as soon as all the caustic soda is neutralised and the normal carbonate is half neutralised, the pink colour will disappear. One may now add methyl orange and continue adding the acid till the neutral tint is attained.

The changes involved may be expressed thus :—

$$NaOH + HCl = NaCl + H_2O \quad . \quad . \quad . \quad (I.)$$
$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \quad . \quad (II.)$$
$$NaHCO_3 + HCl = NaCl + H_2O + CO_2 \quad . \quad (III.)$$
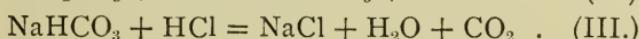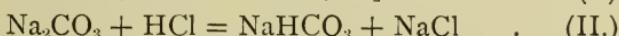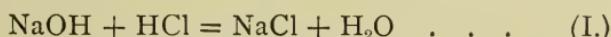
Suppose 20 c.c. of alkali solution were taken and x c.c. of $\frac{N}{10}$ HCl run in before the phenolphthalein lost its colour (stages I. and II.), and y c.c. more acid were required to obtain a neutral reaction to methyl orange (stage III.).

Then $2y$ is number of c.c. required for the carbonate, and $x + y - 2y = x - y$ c.c. are needed for the caustic soda.

The solution thus contains, in a litre—

$$(x - y) \times 0\cdot004 \times \tfrac{1000}{20} \text{ gms. of NaOH}$$
and
$$2y \times 0\cdot0053 \times \tfrac{1000}{20} \text{ gms. Na}_2\text{CO}_3$$

OXIDATION PROCESSES

PREPARATION OF $\dfrac{N}{10}$ POTASSIUM PERMANGANATE.

Potassium permanganate in the presence of dilute sulphuric acid is capable of oxidising a large number of substances in a definite quantitative manner ; the oxidising power is such as may be represented by the following equation :—

$$2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5\text{O}$$
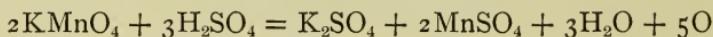
that is, 316 grams of potassium permanganate will yield 80 grams of oxygen. From the considerations set forth on page 46, it will be seen that a $\dfrac{N}{10}$ solution must therefore contain $\tfrac{1}{100}$ of this amount, *i.e.* 3·16 grams.

It is difficult, however, to ensure a solution of potassium permanganate having this exact concentration by weighing out the precise amount and dissolving, as it is extremely sensitive to any small amount of organic matter which may be in the distilled water, or in the flask or bottle to which it is transferred. It is, therefore, better to dissolve about 3·2 grams of potassium permanganate in 1000 c.c. of water, and " standardise " the solution in one of the ways given below, and then use a "factor" instead of attempting to get the solution exactly decinormal. The solution alters slowly if kept, and this standardisation should, therefore, always be made when the solution is used after an interval.

STANDARDISATION OF POTASSIUM PERMANGANATE SOLUTION.

(A) By Iron.

This process depends on the oxidation of ferrous to ferric sulphate by the potassium permanganate—

$$2FeSO_4 + O + H_2SO_4 = Fe_2(SO_4)_3 + H_2O$$
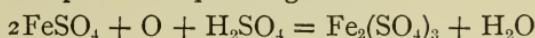
2×56 grams of iron are thus oxidised from the ferrous to the ferric state by 16 grams of oxygen, or 56 grams by 8 grams, *i.e.* the "equivalent" of iron in this reaction is 56.

Combining this result with the equation given on p. 56, it will be seen that 1 c.c. of $\frac{N}{10}$ potassium permanganate will oxidise 1 c.c. $\frac{N}{10}$ Fe or 0·0056 gram of iron.

The standardisation of the permanganate solution can be effected through this reaction in two ways—

(i) by dissolving a known weight of pure iron in sulphuric acid under such conditions as to ensure the absence of any oxidation during the solution.

(ii) by using the definite and comparatively stable salt, ferrous ammonium sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$, which contains exactly $\frac{1}{7}$ its weight of iron.

(i) Pure iron wire is carefully cleaned with fine emery paper, and a quantity of about a gram accurately weighed. About 75 c.c. of sulphuric acid (1 part concentrated acid and 5 parts water) is placed in a round-bottomed flask of 200 c.c. capacity, provided with a cork through which passes a short piece of glass tubing, to the upper end of which is attached a small length of rubber tubing closed by a piece of glass rod, and containing a short clean longitudinal cut about the middle of its length. This acts as a valve.

The acid is boiled for about half a minute so as to expel the air from the flask, the cork removed, and the iron wire dropped in and the cork replaced as quickly as possible. The solution of the wire is accelerated towards the end, if necessary, by again heating the flask. As soon as all the iron has entirely disappeared,

the flask is cooled under the tap, the contents transferred to a standard 250 c.c. flask, and the volume made up to the mark with distilled water, which has been briskly boiled for a few minutes and then cooled as rapidly as possible.

Ten c.c. of this iron solution should be placed in a small flask, and the potassium permanganate solution run in until a permanent faint rose colour is obtained. It is better to ensure the presence of a sufficient amount of sulphuric acid by adding 20 to 30 c.c. of dilute sulphuric acid before commencing to run in the permanganate. If there is not enough sulphuric acid present to form sulphates with the whole of the potassium and manganese in the potassium permanganate, there is obtained a brown precipitate of the higher oxides of manganese; and not only is the end reaction thereby obscured, but the full oxidising effect of the permanganate is not available. Further, the presence of an excess of sulphuric acid checks the reducing action which the manganese sulphate formed in the reaction itself exerts on the potassium permanganate.

After a number of readings have given the amount of potassium permanganate solution which is required to oxidise 10 c.c. of the iron solution, the strength of the permanganate is calculated in the following manner :—

Suppose 1·32 grams of iron had been taken, dissolved in acid and made up to 250 c.c.

10 c.c. of this solution contain $1·32 \times \dfrac{10}{250} = \dfrac{1·32}{25}$ grams of iron, and will therefore require $\dfrac{1·32 \times 8}{25 \times 56}$ grams of oxygen.

Suppose that 9·2 c.c. of permanganate solution had been required for the oxidation of the iron in this 10 c.c.

Then 9·2 c.c. potassium permanganate solution contain

$$\dfrac{1·32 \times 8}{25 \times 56} \text{ grams of oxygen}$$

or   1 c.c.   ,,   ,, $\dfrac{1·32 \times 8}{25 \times 56 \times 9·2}$,,   ,,

or   1 c.c. $= \dfrac{1·32 \times 8}{25 \times 56 \times 9·2 \times 0·0008} \dfrac{\mathbf{N}}{10} \text{ KMnO}_4$

$$= 1·025 \text{ c.c. } \dfrac{\mathbf{N}}{10} \text{ KMnO}_4$$

(ii) Several quantities (about 0·4 gram each) of powdered pure ferrous ammonium sulphate [$(NH_4)_2SO_4 . FeSO_4 . 6H_2O$], dried between filter paper, are weighed out; one of these is dissolved in air-free water (prepared as above), dilute sulphuric acid added (30 c.c.), and the permanganate solution run in until a faint rose colour is permanent. The other quantities of ferrous salt are treated in the same way. Each determination requires a separate calculation; but this method is nevertheless more satisfactory than making a solution of a larger amount of the ferrous ammonium sulphate, and taking fractions of this for the determinations.

Suppose for one determination 0·382 gram of the salt had been used, and 9·1 c.c. of potassium permanganate solution had been required.

0·382 gram ferrous ammonium sulphate contain $\dfrac{0·382}{7}$ grams iron, and 56 grams of iron require 8 grams of oxygen.

∴ 0·382 gram of iron require $\dfrac{8}{56} \times \dfrac{0·382}{7}$ grams of oxygen

∴ 9·1 c.c. potassium permanganate solution contain

$$\frac{8}{56} \times \frac{0·382}{7} \text{ grams of oxygen.}$$

1 c.c.   ,,   ,, $\dfrac{8}{56} \times \dfrac{0·382}{7 \times 9·1}$

or 1 c.c. potassium permanganate solution contains

$$\frac{8}{56} \times \frac{0·382}{7 \times 9·1 \times 0·0008} \text{ c.c. } \frac{N}{10} KMnO_4 = 1·07 \text{ c.c. } \frac{N}{10} KMnO_4$$

(B) By Oxalic Acid.

This method depends on the oxidation of oxalic acid to carbon dioxide and water, according to the equation—

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} .2H_2O + O = 2CO_2 + 3H_2O$$
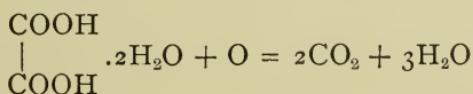
From this reaction the "equivalent" of oxalic acid (crystallised) is 63, and a decinormal solution will therefore contain 6·3 grams in 1000 c.c.

$\dfrac{N}{10}$ oxalic acid is then prepared by dissolving 6·3 grams of pure crystallised oxalic acid in water and making up to 1000 c.c.

Ten c.c. of this solution should then be placed in a small flask, and 30 c.c. of dilute sulphuric acid added. A couple of c.c. of permanganate is then run in, and the mixture gently heated until the colour of the permanganate disappears. No further heating is usually necessary, but further additions of permanganate are reduced as long as any oxalic acid remains.

Suppose 9·8 c.c. are required ; this amount, then, is equivalent to 10 c.c. $\dfrac{N}{10}$ oxalic acid, *i.e.* is equal to 10 c.c. $\dfrac{N}{10}$ KMnO$_4$

$$\left.\begin{array}{l}\therefore \text{ 1 c.c. potassium}\\ \quad\text{permanganate solution}\end{array}\right\} = \dfrac{10}{9\cdot8}\ \text{c.c. }\dfrac{N}{10}\,\text{KMnO}_4$$

$$= 1\cdot02\ \text{c.c. }\dfrac{N}{10}\,\text{KMnO}_4$$

The potassium permanganate, after being standardised by one of the above methods, can now be used to determine the amount of **oxalate,** or the amount of **ferrous iron** present in a given solution or solid. The experimental details are the same as in the case of standardisation of the permanganate.

The permanganate can also be used to determine **ferric iron ;** in this case the substance is dissolved in dilute sulphuric acid (1 in 6), or sulphuric acid is added to the solution so as to give roughly 1 volume of concentrated sulphuric acid in 6 volumes of the mixture, and the ferric iron reduced to ferrous iron by addition of magnesium, or specially pure iron-free zinc, or by saturating with sulphuric dioxide, and subsequently heating to expel all the excess of sulphuric dioxide.

The completion of the reduction is indicated by the absence of any pink colour when a drop of the solution is added to a spot of ammonium thiocyanate solution on a white glazed tile.[1]

The ferrous iron is then estimated as before.

[1] The reduction of ferric to ferrous iron can be quickly and easily accomplished by the following process :—

A solution of the ferric salt is made by dissolving such a weight in 500 c.c.

By first estimating the iron present in the ferrous condition, and then reducing a separate portion, and estimating the total iron, it is possible to find the amounts of iron present in both ferrous and ferric states.

ESTIMATION OF HYDROGEN PEROXIDE.

Hydrogen peroxide can be estimated by means of potassium permanganate, as the " nascent " oxygen given by the latter reacts with the hydrogen peroxide as shown by the equation—

$$H_2O_2 + O = H_2O + O_2$$
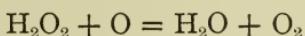
1 litre of $KMnO_4$ is therefore equivalent to $\frac{1}{2}(H_2O_2) = 17$ grams of hydrogen peroxide, *i.e.* 1 c.c. $\frac{N}{10} KMnO_4 = 0.0017$ gram of hydrogen peroxide.

If the strength of the solution is totally unknown, some of it may be diluted to 5 times the volume, the concentration of this diluted solution found roughly, and if the dilution is not such as to need from 8 to 12 c.c. of the permanganate solution per 10 c.c. of the diluted hydrogen peroxide, a fresh quantity of the original solution is taken and diluted so as to give a concentration needing from 8 to 12 c.c. of the permanganate for 10 c.c. The process of titration is exactly the same as in estimating ferrous iron ; the solution must **not** be heated.

ESTIMATION OF CALCIUM.

Calcium can be estimated by precipitation as oxalate, and determination of the oxalate by means of potassium permanganate solution.

Precipitate the calcium in ammoniacal solution with ammonium

of 1 in 6 sulphuric acid as will give an approximately $\frac{N}{10}$ solution when reduced. 20 c.c. of the solution is taken and a *large* quantity of zinc added, and the solution heated. Reduction is soon complete, and then, without waiting for the zinc to be dissolved, 200 c.c. of a saturated solution of mercuric chloride is added, and the mixture rapidly cooled. The action is thereby stopped, and the permanganate may be run in to the mixture directly.

oxalate, thoroughly wash the precipitate, then transfer to a titration flask with water, add excess of diluted H_2SO_4, and titrate the liberated oxalic acid. The calcium sulphate formed does not interfere with the titration.

Exercises.—Estimation of ferrous iron in given solutions $\left(\dfrac{N}{20} \text{ to } \dfrac{N}{5}\right)$

Estimation of ferrous iron in ferrous sulphate, "reduced iron," ferrous ammonium sulphate.

Estimation of ferric iron in iron ammonium alum.

Estimation of ferrous and ferric iron in crude green vitriol.

Estimation of oxalic acid in given solutions $\left(\dfrac{N}{20} \text{ to } \dfrac{N}{5}\right)$.

Estimation of "oxalate" in potassium hydrogen oxalate, potassium oxalate.

Estimation of hydrogen peroxide 20 vol., 10 vol.

Note.—The facts to be borne in mind in all these determinations are—

(1) That 1 c.c. $\dfrac{N}{10}$ $KMnO_4$ yields 0·0008 gram of oxygen.

(2) That 1 c.c. $\dfrac{N}{10}$ $KMnO_4$ will therefore oxidise $\dfrac{1}{10,000}$ of the equivalent of the substance oxidised, regard being given to the reaction which is taking place.

PREPARATION AND USE OF DECINORMAL
POTASSIUM DICHROMATE.

Potassium dichromate, like potassium permanganate, is an oxidising agent in the presence of acid. It has the advantage that it can be used with hydrochloric acid, and it is therefore frequently used in the estimation of iron present in the form of chloride.

In this reaction, however, the deep green colour of the chromium salt produced obscures to some extent the end point of the reaction, and, though after a little experience it is fairly easy to tell when the dichromate is just in excess (through the brownish tint then shown), an external indicator is therefore often used. This is afforded by a solution of potassium ferricyanide, which must be freshly prepared from the solid

immediately before use; potassium ferricyanide gives blue or green with even a trace of ferrous salt, but only an olive colour with ferric salts.

The use of potassium dichromate depends, again, on the liberation of oxygen in the presence of acids and oxidisable material, as represented by the equation—

$$K_2Cr_2O_7 + 8HCl = 2KCl + Cr_2Cl_6 + 4H_2O + 3O \;[1]$$
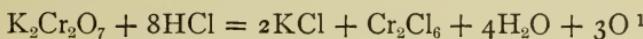
The "equivalent" of potassium dichromate is therefore $\dfrac{K_2Cr_2O_7}{6} = 49$. About 10 grams of potassium dichromate should be finely powdered, and then gently heated on an iron dish until the whole mass is just fused. The salt is then allowed to cool in a desiccator, broken up, and once more finely powdered. A quantity of exactly 4·9 grams is weighed, dissolved in water, and made up to 1000 c.c.

ESTIMATION OF FERROUS IRON.

The ferrous compound is dissolved in water so as to give a solution approximately decinormal—if a totally unknown substance is given, a solution can be made up, its strength determined roughly (as below), and an appropriate solution then prepared by dilution or by starting afresh from the solid substance.

Ten c.c. of the ferrous solution should then be placed in a small flask, and potassium dichromate run in from a burette. From time to time, more frequently towards the end of the reaction, a drop of the solution is taken out of the flask by means of a rod, and the drop is allowed to mix with a spot of potassium ferricyanide on a glazed white tile.[2] When the resulting mixture no longer shows a tinge of green, the process is complete and a reading is taken. This gives only a rough value. The process

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[1] **Note for Student.**—When potassium dichromate and hydrochloric acid are heated together, chlorine is evolved : account for this.

[2] The student is advised to perform this estimation without the use of the indicator (*cf.* p. 62) as well as by the method here described.

is repeated, the dichromate being now run in quickly till a volume near to the result just obtained has been added, and then slowly testing as before. Determinations are made till three successive readings are in fair agreement. The calculation is similar to that for potassium permanganate.

ESTIMATION OF FERRIC IRON.

Ferric iron, and mixtures of ferrous and ferric iron, can be estimated by potassium dichromate in the same way as in the case of potassium permanganate; the reducing agent in this case may be zinc and hydrochloric acid or stannous chloride, there being no longer any objection to the use of chlorides. (*Cf.* page 60.)

Note.—1 c.c. $\frac{N}{10}$ $K_2Cr_2O_7$ gives 0·0008 gram of oxygen, and oxidises 0·0056 gram of iron from ferrous to ferric state.

ESTIMATION OF THIOSULPHATES.

Potassium dichromate can be used to estimate thiosulphates in solution or to standardise sodium thiosulphate solution, by the aid of potassium iodide.

Ten c.c. of $\frac{N}{10}$ $K_2Cr_2O_7$ is mixed with dilute sulphuric acid and excess of potassium iodide solution, and the thiosulphate run in until the iodine is completely decolorised. The strength of the thiosulphate can then be easily calculated, as 1 c.c. of $\frac{N}{10}$ $K_2Cr_2O_7$ liberates 0·0127 gram of iodine. (See below.)

IODINE AND SODIUM THIOSULPHATE.

On the use of one or other, or a combination, of these two substances, many useful methods of volumetric analysis depend, a few of which are here given.

Iodine is usually an oxidising agent, and it is on this property that most of the reactions utilised depend. It reacts with sodium thiosulphate thus—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6 \text{ (sodium tetrathionate)}.$$
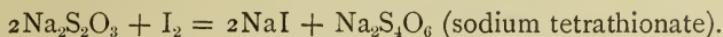
The equivalent of sodium thiosulphate, in respect to this reaction, is therefore $\dfrac{2Na_2S_2O_3}{2}$; or for the crystallised substance, $Na_2S_2O_3 \cdot 5H_2O, = 248$.

PREPARATION OF DECINORMAL SODIUM THIOSULPHATE.

For all ordinary purposes commercial sodium thiosulphate of good quality may be used without any purification or standardisation, if the solution is freshly prepared. If it is considered desirable for any reason to standardise the thiosulphate, this may be done either by $\dfrac{N}{10}$ potassium dichromate (p. 64) or by $\dfrac{N}{10}$ iodine, either prepared from resublimed iodine or previously rendered accurate by titration with arsenious oxide solution (p. 66). Some 50 grams of the crystallised salt should be finely powdered and dried by pressing between filter papers. Of this a weight of exactly 24·8 grams should be dissolved in air-free water (p. 58) and made up to 1000 c.c.

This solution may be standardised as suggested above ; this should always be done before use, if the thiosulphate solution is not freshly prepared, as it does not keep well.

PREPARATION OF DECINORMAL IODINE.

This can be prepared by dissolving 12·7 grams of resublimed iodine in a solution of 35 grams potassium iodide in **not more** than 40 c.c. of water and diluting, *after all the iodine is dissolved,*

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to 1000 c.c. It is important to note that the solubility of iodine depends on the concentration of the potassium iodide. A given weight of potassium iodide dissolves less iodine the more dilute the solution; once the iodine is dissolved it is not so easily thrown out of solution again by dilution.

It is, however, better not to depend on the iodine solution as absolute, but to standardise with $\frac{N}{10}$ thiosulphate, or $\frac{N}{10}$ arsenious acid. It is also much more economical, as ordinary commercial iodine can then be used instead of the even more costly resublimed substance.

A quantity of crude iodine of about 13 grams is weighed, dissolved in 35 grams of potassium iodide in 40 c.c. of water, and diluted to 1000 c.c.

Ten c.c. of this solution are placed in a small flask, and $\frac{N}{10}$ thiosulphate run in until the brown colour has faded to a pale yellow. One c.c. of a very dilute solution of starch (see under Indicators) is added, and the thiosulphate run in until the intense blue colour just disappears. The calculation is as follows :—

Suppose the volume of $\frac{N}{10}$ thio. required were 10·2 c.c.

10 c.c. iodine solution = 10·2 c.c. $\frac{N}{10}$ thio. = 10·2 c.c. $\frac{N}{10}$ iodine,

1 c.c. iodine solution = 1·02 c.c. $\frac{N}{10}$ iodine.

Or, 10 c.c. of the iodine solution are placed in a small flask, 20 c.c. of a concentrated solution of sodium bicarbonate (free from any trace of carbonate) added, and $\frac{N}{10}$ arsenious acid solution run in till the brown colour has faded to a pale yellow, 1 c.c. of starch solution (see under Indicators) added, and the $\frac{N}{10}$ As_2O_3 run in until the intense blue just disappears. The calculation is as before.

If 10·2 c.c. $\dfrac{N}{10}$ As$_2$O$_3$ were required,

$$10 \text{ c.c. iodine} = 10 \cdot 2 \text{ c.c. } \dfrac{N}{10} \text{ iodine,}$$

i.e. 1 c.c. iodine = 1·02 c.c. $\dfrac{N}{10}$ iodine.

The arsenious acid solution is prepared by dissolving 4·95 grams of pure arsenious oxide in about half a litre of a saturated solution of pure sodium bicarbonate (free from carbonate) and making up to 1000 c.c. The vitreous form of the oxide should be avoided, as it is much less soluble even in the presence of bicarbonate. For the reaction involved, see below.

ESTIMATION OF ARSENIC OR ANTIMONY.

Iodine reacts with arsenious oxide or antimony trioxide according to the equations

$$As_2O_3 + 2H_2O + 4I = As_2O_5 + 4HI$$
$$Sb_2O_3 + 2H_2O + 4I = Sb_2O_5 + 4HI$$
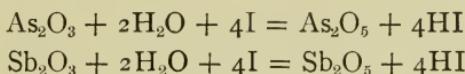
These reactions are reversible, and it is necessary (in order to ensure their completion in the way desired) to remove the hydriodic acid from the "sphere of action." This cannot be effected by caustic soda or normal carbonate, as these have themselves an action with iodine. It is therefore necessary to use pure sodium bicarbonate, which removes the hydriodic acid, forming iodide, carbon dioxide, and water, but has no action on iodine.

The process of the estimation is, in either case, the same as described for the standardisation of iodine solution. The arsenious or antimonious compound, if given in the solid form, is dissolved in water (or sodium bicarbonate solution) to form an approximately decinormal solution (*cf.* p. 61), and the solution run into 10 c.c. of iodine (1 c.c. = 1·02 c.c. $\dfrac{N}{10}$ iodine) until the

reaction is finished (see above). Suppose the amount required
was 9·6 c.c.

$$9·6 \text{ c.c. required } 10 \text{ c.c. iodine} = 10·2 \text{ c.c. } \frac{N}{10} \text{ iodine}$$

$$\therefore 9·6 \text{ c.c.} = 10·2 \text{ c.c. } \frac{N}{10} As_2O_3, \text{or } \frac{N}{10} Sb_2O_3$$

$$1 \text{ c.c.} = \frac{10·2}{9·6} = 10·63 \text{ c.c. } \frac{N}{10} As_2O_3, \text{or } \frac{N}{10} Sb_2O_3$$

Also 1 c.c. of $\frac{N}{10} As_2O_3$ contains 0·00495 gram arsenious oxide,
and 1 c.c. of $\frac{N}{10} Sb_2O_3$ contains 0·0072 gram antimony trioxide.

From these data, the percentage of As_2O_3 or Sb_2O_3 can be
easily calculated.

Exercises.—Estimation of the amount of As_2O_3 in given solutions
$\left(\frac{N}{20} \text{ to } \frac{N}{5}\right)$.

Estimation of the amount of Sb_2O_3 in given solutions $\left(\frac{N}{20} \text{ to } \frac{N}{5}\right)$.

Estimation of the percentage of Sb_2O_3 in tartar emetic.

Note.—The estimations can be made by adding excess of iodine and
titrating the excess by $\frac{N}{10}$ thio.

The number of c.c. of the $\frac{N}{10}$ thio. solution is then subtracted
from the number of c.c. of the $\frac{N}{10}$ iodine solution, and the calculation
continued as above.

ESTIMATION BY MEANS OF POTASSIUM IODIDE

Many oxidising substances liberate iodine from acidified
solutions of potassium iodide, and can be estimated by titrating
the iodine so liberated with $\frac{N}{10}$ of thiosulphate solution. Examples
are afforded by bleaching powder and hydrogen peroxide. Other

substances, *e.g.* manganese dioxide, will yield chlorine on heating with concentrated hydrochloric acid ; the chlorine may be passed into a concentrated solution of potassium iodide, and the liberated iodine estimated in the usual manner.

The general methods of procedure are essentially the same for all substances of the same class, and it will be sufficient to select a typical case of each.

(A) Example of a substance which will act directly with potassium iodide solution. Estimation of available chlorine in bleaching powder.

A solution of the sample of bleaching powder to be estimated is made by thoroughly grinding with about 50 c.c. of water 20 grams of the substance (weighed as rapidly as possible) ; the water should be added gradually. The result of the grinding should be a fairly thin even cream without any lumps. About 200 c.c. of water should now be added, the whole stirred well and allowed to settle ; the clear supernatant liquid is then poured off through a filter paper into a litre flask, the residue treated again with a further 200 c.c., stirred well, allowed to settle, and the clear liquid again transferred through the filter to the litre flask. The process is repeated twice more, and the contents of the flask then made up to the mark and thoroughly mixed.

Twenty c.c. of this bleaching powder solution should then be transferred to a titrating flask (100 c.c. capacity), 20 c.c. of a 10 per cent. solution of potassium iodide added, and 20 c.c. of dilute hydrochloric acid. The iodine liberated is then estimated by $\frac{N}{10}$ thio., as described above. The calculation may be made as follows :—

Suppose 18·86 grams of bleaching powder had been taken, and 1000 c.c. of solution obtained, and that 20 c.c. of this solution, after adding 20 c.c. of potassium iodide, required 21·6 c.c. of $\frac{N}{10}$ thio. to react with the iodine.

$$1 \text{ c.c. } \frac{N}{10} \text{ thio.} = 0.0127 \text{ gram I} = 0.00355 \text{ gram Cl}$$

$$21.6 \text{ c.c. } \frac{N}{10} \text{ thio.} = 0.00355 \times 21.6 \text{ grams Cl}$$

∴ 20 c.c. bleaching powder solution yields 0.00355×21.6 gms. Cl

1000 c.c.   ,,   ,,   ,,   ,, $0.00355 \times 21.6 \times 50$,,

18.86 grams bleaching powder yield $0.00355 \times 21.6 \times 50$,,

Percentage of "available chlorine" $= \dfrac{0.00355 \times 21.6 \times 50 \times 100}{18.86}$

$$= 20.33$$

(B) Example of a substance yielding chlorine when heated with concentrated hydrochloric acid. Estimation of manganese dioxide in pyrolusite.

When manganese dioxide is heated with hydrochloric acid, chlorine is evolved according to the action expressed in the following equation :—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$
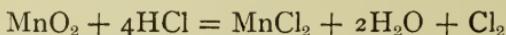
from which it will be seen that the amount of chlorine evolved is the chemical equivalent of the " available " oxygen in the manganese dioxide, or of the amount of pure MnO_2 in a sample of crude material. The chlorine so evolved is absorbed by a solution of potassium iodide, whereby an amount of iodine chemically equivalent to the chlorine is liberated and may be estimated by a standard solution of sodium thiosulphate.

Suppose that it is required to find the percentage of true MnO_2 in a sample of pyrolusite. One should proceed as follows :—

Place about $\frac{1}{2}$ gram of the pyrolusite (in fine powder) in a flask of about 100 c.c. capacity, provided with a delivery tube which is fitted to the flask by means of a cork or rubber stopper. Should a cork be used, it must be well soaked in paraffin; if a rubber stopper is employed, it should be previously boiled in caustic soda to remove sulphur.

The delivery tube passes, as shown in the photograph, into a set of absorption tubes containing potassium iodide solution (10 grams of potassium iodide in about 30 c.c. of water for $\frac{1}{2}$ gram of pyrolusite).

Place in the flask along with the pyrolusite a few fragments of magnesite, and then pour in from 25 to 30 c.c. of concentrated hydrochloric acid. The magnesium carbonate is only slowly attacked by the acid, and serves to furnish a slow current of carbon
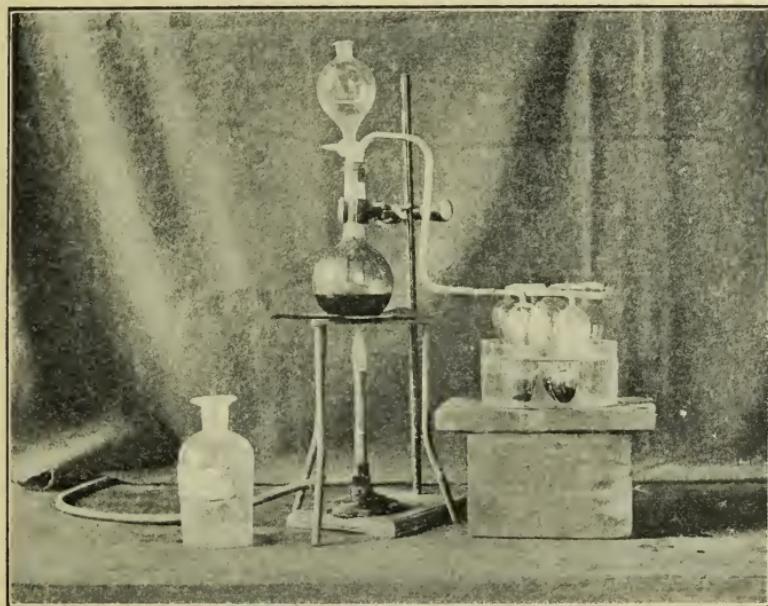

FIG. 15.

dioxide, which sweeps out the chlorine and also prevents the solution of potassium iodide from being sucked back towards the end of the reaction.

Warm the flask and its contents; chlorine will be evolved, and, on entering the absorption bulbs, will be entirely absorbed by the iodide, with liberation of iodine. When the manganese dioxide is completely decomposed, heat the liquid in the flask to boiling and continue the boiling for a few minutes. The gas in the flask and delivery tube should now be perfectly free from any green tint.

Now transfer the liquid in the absorption bulbs to a measuring flask of 100 c.c. capacity, carefully washing out the bulbs with distilled water, and fill up to the mark with water, and thoroughly mix. Withdraw 25 c.c. by means of a pipette and estimate the iodine by means of a decinormal solution of sodium thiosulphate.

Enter your results thus :—

Weight of pyrolusite taken $\quad = a$ grams.

25 c.c. of the iodine solution

obtained required $\dfrac{N}{10}$ thio. $\quad = b_1$ c.c.

$\quad$,, $\quad$ (2nd determination) $= b_2$,,

$\quad$,, $\quad$ (3rd $\quad$,, $\quad = b_3$,,

$\quad$ mean $= \dfrac{b_1 + b_2 + b_3}{3} = b$,,

Now, 1 c.c. of $\dfrac{N}{10}$ thio. $= 0.0127$ gram $I = 0.00355$ gram Cl

$= 0.008$ gram $O = 0.00435$ gram MnO_2

as shown in the equations

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$
$$2KI + Cl_2 = 2KCl + 2I$$
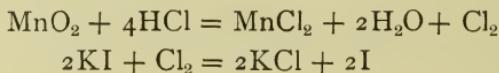
Hence percentage of manganese dioxide in the sample of pyrolusite $= \dfrac{4 \times b \times 0.00435 \times 100}{a}$

ESTIMATION OF CHLORIDE IN SOLUTION BY STANDARD SILVER NITRATE.

The estimation is based upon the reaction expressed by the following equation :—

$$AgNO_3 + NaCl = AgCl + NaNO_3$$
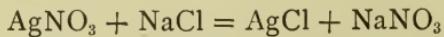
A similar reaction occurs with any soluble chloride and with any soluble salt of silver.

To prepare a standard solution of silver nitrate, dissolve 17 grams of this salt in one litre of water ; this will give a deci-normal solution, and as silver nitrate of a high degree of purity

can be obtained, the solution thus made may be generally used without further standardisation. If necessary, its strength can be determined by means of a standard solution of pure sodium chloride. The sodium chloride is prepared according to the method described on p. 40, and 5·85 grams of the dry salt should be very accurately weighed and dissolved in a litre of water (or quantities proportional to these).

The silver nitrate solution is placed in a burette, and the standard sodium chloride in a beaker. The silver nitrate solution is then run into the chloride until precipitation is complete, this point being easily determined if a few drops of a solution of neutral potassium chromate be added. As soon as all the chloride has been thrown down, a permanent red colour, due to the formation of silver chromate, is produced. Neutral potassium chromate is, therefore, the indicator used in this estimation. The solution of silver nitrate should then be adjusted, if necessary, until any given volume will exactly precipitate an equal volume of the standard sodium chloride, when, as will be seen from the equation, 1 litre precipitates 3·55 grams of chlorine, *i.e.* 1 c.c. is equivalent to 0·00355 gram Cl.

The solution should be kept in a blackened or dark brown bottle.

The method of estimating a chloride will be the same as that adopted for the standardisation of the silver nitrate. About 4 grams of the chloride should be weighed accurately and dissolved in 500 c.c. of water. Twenty c.c. of the solution should then be placed in a beaker with a few drops of potassium chromate, and the silver nitrate run in until the red colour of the silver chromate is just permanent.

The calculation will be as follows :—

Let m be the weight of chloride taken and dissolved in 500 c.c. of water, and v the volume in c.c. of $\frac{N}{10}$ silver nitrate required.

Then the amount of chlorine present in 20 c.c. of the chloride solution is $v \times 0\cdot00355$, and in the entire 500 c.c. of solution is $v \times 0\cdot00355 \times 25$, *i.e.* in m grams of the chloride : therefore the amount per cent. is $\dfrac{v \times 0\cdot00355 \times 25 \times 100}{m}$

The same method can be employed for the estimation of bromide and iodide, remembering that 1 c.c. of the standard silver nitrate will be equivalent to 0·008 gram of bromine and 0·0127 of iodine.

ESTIMATION OF CYANIDE IN SOLUTION BY STANDARD SILVER NITRATE.

The solution of hydrocyanic acid or cyanide is first rendered alkaline, if necessary, with caustic potash or soda, and standard solution of silver nitrate is added.

In this estimation no indicator is necessary, as during the reaction a soluble double cyanide of silver and potassium is produced, and no precipitate is formed until the silver solution has been added in quantity in excess of that required for the formation of the soluble double cyanide, when a white precipitate of silver cyanide is formed. The reactions are expressed by the following equations :—

$$2KCN + AgNO_3 = \underbrace{KCN \,.\, AgCN}_{\text{sol. double cyanide}} + KNO_3$$

$$KCN \,.\, AgCN + AgNO_3 = 2\,AgCN + KNO_3$$
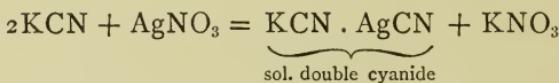
The appearance of the white precipitate indicates the end of the first stage of the reaction, and this is quite sufficient to determine the amount of cyanide present ; at this stage of the reaction, every 1 c.c. of $\frac{N}{10}$ silver nitrate solution used indicates the presence of 0·0052 of cyanide radicle (CN).

EXERCISES IN GRAVIMETRIC ANALYSIS

THE student should perform a sufficient number of the following simple exercises to acquire confidence in the accuracy of his results. For this purpose it is better for him to make several determinations on pure specimens, before passing on to estimate the composition of crude materials. The paramount importance of reliability must be recognised at the earliest stages, and it is far preferable to perform a few estimations carefully than a large number in a slip-shod manner.

The examples given below have been selected as typical of the more important general methods of gravimetric analysis, but further practice may be obtained if necessary, as suggested in the text.

General Note.—In all the following exercises the student should weigh in grams accurately to three places of decimals, and to ensure accuracy thus far, it is advisable to weigh to the fourth place of decimals, that is to $\frac{1}{10}$ milligram.

ANALYSIS OF COPPER SULPHATE.

1. Estimation of Water of Crystallisation.

A clean porcelain crucible, with lid, is heated in the flame of a bunsen burner for five or ten minutes, allowed to cool in a desiccator, and weighed. A quantity of powdered crystallised copper sulphate (about $1\frac{1}{2}$ grams) is placed in the crucible, and the weight accurately determined.

The crucible is now heated for half an hour over a small bunsen flame, the tip of which should be about $\frac{1}{2}$ inch below the bottom of the crucible. It is then allowed to cool in a

desiccator and weighed. The crucible is again heated for the space of ten minutes, and once more cooled in a desiccator and weighed. If this last weight is the same as that after the first heating, it may be taken as the final weight, but if there has been a second loss in weight, the heating must be repeated, until two successive weighings do not differ by more than 0·3 of a milligram.

The results should be entered in this form :—

Weight of crucible + lid . . . . $= a$
Weight of   ,,   ,, + copper sulphate   . . $= b$
Weight of copper sulphate taken   . . . . . . $= b - a$
Weight of crucible + lid + residue after 1st heating $= c_1$
Weight of   ,,   ,,   ,,   ,,   2nd   ,, $= c_2$
Weight of   ,,   ,,   ,,   ,,   3rd   ,, $= c$ const.

Percentage of water of crystallisation $= \dfrac{(b - c) \times 100}{b - a}$

2. Estimation of Copper.

Some of the powdered copper sulphate (between 0·5 and 1·0 gram), is accurately weighed and dissolved in about 150 c.c. of distilled water, with the addition of a drop of sulphuric acid, if necessary ; the solution is heated to the boiling point and a 10 per cent. solution of caustic soda slowly added, the temperature being maintained near the boiling point until the precipitate is entirely black and the liquid colourless. The precipitate is allowed to settle and the supernatant liquid decanted off through a filter paper : 50 to 100 c.c. boiling water is added to the residue in the beaker, the whole well stirred and allowed to settle.

The clear liquid is again poured off through the same filter paper, and the process of "washing by decantation" repeated three or four times with fresh quantities of boiling water. Finally the precipitate is transferred to the filter paper, and washed with boiling water until the last washings have no effect on red litmus paper or barium chloride solution. (Why is the filtrate tested with these reagents ?)

Some care must be taken in transferring the precipitate to the filter and in the subsequent washing, and for these purposes a

wash bottle containing boiling water will be found useful. It is
convenient to protect the neck of the bottle either with string or
sheet indiarubber, or it will be too hot to handle comfortably.

To transfer the precipitate, the beaker, the lip of which has
been greased on the outside with vaseline, should be held over
the centre of the funnel, mouth downwards, in a steeply inclined
position, and a stream of hot water projected up from the jet
of the wash bottle ; the water on descending will bring down
nearly the whole of the precipitate, which can be guided into
the funnel by means of a glass rod held in contact with the
greased lip of the beaker. No difficulty will be experienced
in holding the glass rod in position with the same hand as
supports the beaker. Should any precipitate remain on the
sides of the beaker, it can be removed by means of a small
piece of indiarubber tubing fixed on the end of a glass rod.
The small amount of precipitate on the glass rod and rubber
must, of course, be carefully washed into the funnel with a jet
of hot water. The precipitate, when upon the filter paper, is
further washed by the addition of hot water, each quantity
being allowed to drain away before the next is added.

Note.—The filter paper must never be more than three-quarters full, or
there will be a danger of the precipitate creeping over the edge.

The process can be accelerated in this, and all cases, by
the use of the filter pump. If the pump is used the filter should
be strengthened by a small cap of " hardened " filter paper,
through which a few *fine* holes may be made, or one of linen,
and great care must be taken that the filter paper fits closely and
evenly to the filter.

After washing, the funnel containing the filter paper and
precipitate is transferred to the steam oven, dried, and as much
of the precipitate as possible removed and placed in a dried
weighed crucible standing on a piece of hard glazed paper.

The filter is now taken out of the funnel, opened, and folded
in half ; it will then be found that gentle rubbing of the two
halves of the filter paper against one another will detach the
bulk of the precipitate from the paper, and it can be run down

the fold of the paper into the crucible. A camel-hair pencil may be found useful in guiding the precipitate, and in removing the last loose portions.

The paper should now be folded into a narrow wedge, held by one corner in a pair of clean crucible tongs, set on fire, and allowed to burn quietly over the crucible containing the precipitate.

As soon as the burning is completed, a slight tap will remove the bulk of the filter ash, containing what was left of the precipitate into the crucible. The rest of the ash and small portion of unburnt filter paper can then be added, and the whole heated strongly over a bunsen burner. If the precipitate has been properly washed, it will not have reached the edge of the filter paper, and any small fragment of paper sticking to the tongs can be ignored, the weight of its ash being quite negligible.

An alternative procedure is to fold up the filter paper, from which most of the precipitate has been removed, into small compass and coil round it, so as to form a cage, a length of platinum wire, leaving about 3 inches to take hold of. The paper is held in the bunsen flame until alight, and allowed to burn quietly over the crucible until all glow has ceased; the flame is then directed upon it to complete the combustion, and the ash allowed to drop into the crucible.

The crucible and contents are then heated until the incineration is complete, allowed to cool, and two or three drops of concentrated nitric acid added (to oxidise any copper which may have been reduced by the carbonised filter paper), and again heated in order to convert into oxide the copper nitrate produced.

The crucible and contents are allowed to cool in the desiccator and weighed.

The results may be entered thus :—

Weight of copper sulphate taken . . . . $= m$
Weight of crucible . . . . $= a$
Weight of crucible $+$ CuO $+$ ash . . . . $= b$
Weight of ash (given by makers of filter paper) $= c$

$$\text{Percentage of copper} = \frac{63 \cdot 5}{79 \cdot 5} \times (b - a - c) \times \frac{100}{m}$$

3. Estimation of Sulphate.

A quantity of the powdered copper sulphate, about $\frac{3}{4}$ of a gram, is accurately weighed, dissolved in 100 c.c. of water, with the addition of a few drops of pure hydrochloric acid, and the solution raised to boiling point. A boiling solution of barium chloride is added until the addition of a little more produces no further precipitate. The mixture is then boiled for a minute or two, and allowed to settle. The procedure is then exactly similar to that in the case of the copper estimation above, only the washings must be tested with silver nitrate solution (why?), and one or two special precautions must be taken for a successful result. The barium sulphate often passes very readily through filter paper, and a specially grained paper is therefore advisable : for the same reason care must be taken in using the filter pump, especially during the first stages of the filtering.

Further, by the action of the carbon of the filter paper while burning, a little of the barium sulphate is reduced to sulphide. It is, therefore, necessary to treat the residue after all the black carbon has been burnt, with two or three drops of nitric acid, gently warm, and then add two drops of dilute sulphuric acid, and drive off the excess of the acids by very gentle heating. After the fumes have ceased the crucible and contents should be heated over the bunsen burner, but not above dull redness.

The results may be entered as follows :—

Weight of copper sulphate taken . $= m$
Weight of crucible . . . . . $= a$
Weight of crucible and BaSO$_4$ + ash $= b$
Weight of ash . . . . $= c$

Percentage SO$_4$ in copper sulphate $= \dfrac{96}{233} \times (b - a - c) \times \dfrac{100}{m}$

The final results of the analysis should be tabulated as follows :—

                                                        Per cent.
    Water of crystallisation   .   .   .   .
    Copper . . . .
    Sulphate (SO_4)   . . . . . .

ESTIMATION OF CHLORINE IN CHLORIDES, AS SILVER CHLORIDE.

About $\frac{3}{4}$ of a gram of barium chloride is weighed carefully and placed in a flask of about 300 c.c. capacity—a flask of conical form is preferable—and dissolved in 100 c.c. of cold distilled water containing a little dilute nitric acid. A solution of silver nitrate is then added, the solution heated nearly to boiling, and after allowing the precipitate to settle, a further quantity of silver nitrate solution added, and the mixture again heated. This process is repeated until the addition of more silver nitrate solution produces no turbidity. The precipitate is treated in the usual way, *i.e.* washed by decantation, and on the filter (until the washings are free from salts of silver), and then dried in the steam oven. As much as possible of the silver chloride precipitate is removed from the filter paper into a tared crucible, and heated over a small flame until the silver chloride shows signs of melting, which will be first noticeable at the edges. The crucible is allowed to cool in a desiccator and weighed.

While this operation is in process, the filter paper with the adhering silver chloride should be folded and burnt in the usual manner, but it must be noted that the carbon of the filter paper will cause the decomposition of the silver chloride, and the whole of the precipitate mixed with the ash will then be metallic silver. This, together with the filter ash, is allowed to fall into the crucible, and the crucible and its contents again weighed. The additional weight will be due to the metallic silver, which was

first combined with chlorine, but reduced by the carbon of the filter paper, and to the filter ash; but as the latter, when the specially prepared filter papers are used, is very small, it can generally be neglected, and the increase in weight considered to be due to silver only.

Remembering that 108 parts by weight of silver combine with 35·5 of chlorine, the amount of precipitated silver chloride represented by the silver residue can easily be calculated, and added to the weight of the silver chloride in the crucible. This will give the weight of silver chloride precipitated.

The results should be entered thus:—

Weight of barium chloride taken $\ldots \ldots = m$

Weight of crucible $\ldots \ldots \ldots \ldots = a$

Weight of crucible and silver chloride $\ldots = b$

Weight of silver chloride $\ldots \ldots \ldots = b - a$

Weight of crucible + silver chloride + silver

$\qquad$ + ash $\ldots \ldots \ldots \ldots \ldots = d$

Weight of ash $\ldots \ldots \ldots \ldots \ldots = c$

Weight of silver $\ldots \ldots \ldots \ldots = d - b - c$

Equivalent to silver chloride $= \dfrac{(d - b - c) \times 143\cdot5}{108}$

Total weight of silver chloride

$$= b - a + \frac{(d - b - c) \times 143\cdot5}{108}$$

Percentage of chlorine

$$= \frac{35\cdot5}{143\cdot5} \times \left(b - a + \frac{(d - b - c) \times 143\cdot5)}{108} \right) \times \frac{100}{m}$$

An alternative method is to reconvert the silver into silver chloride, as follows: after allowing the filter ash and silver to fall into the crucible, about three drops of concentrated nitric acid is added (this will dissolve the silver with the formation of silver nitrate): then about the same amount of concentrated hydrochloric acid is dropped in, causing the precipitation of the silver as chloride. The crucible and its contents are dried and afterwards heated to incipient fusion of the chloride as above described, and again weighed.

The results should be entered as below :—

Weight of barium chloride taken . . . .   = m

Weight of crucible . . . .   = a

Weight of crucible + silver chloride and ash   = b

Weight of ash . . . .   = c

Percentage of chlorine $= \dfrac{35\cdot5}{143\cdot5} \times (b - a - c) \times \dfrac{100}{m}$

ANALYSIS OF BARIUM CHLORIDE.

1. Water of crystallisation.—The process is that given under copper sulphate, page 75.

2. Chlorine.—The process is as given on page 80.

3. Barium.—The barium can be estimated by the same process as detailed under copper sulphate, estimation of sulphate. In this case, hot dilute sulphuric acid, or ammonium sulphate solution, is added to the boiling solution of the barium chloride, until no further precipitation occurs, and the washing of the precipitate continued until the water passes through the filter free from chloride.

The result, after proceeding as directed on p. 79, must be tabulated thus :—

Weight of barium chloride . . . . .   = m

Weight of crucible . . . .   = a

Weight of crucible + $BaSO_4$ + ash . . .   = b

Weight of ash . . . .   = c

Percentage barium in barium chloride

$$= \frac{137}{233} \times (b - a - c) \times \frac{100}{m}$$

ESTIMATION OF CALCIUM.

A quantity of pure calcite (Iceland spar), about $\frac{1}{2}$ a gram, is accurately weighed out, and dissolved in a small quantity of moderately dilute hydrochloric acid ; the solution is boiled to expel carbon dioxide, and made alkaline with ammonia. Then ammonium oxalate solution is added to the hot solution till no further

precipitation occurs, and the mixture allowed to stand for one hour. The precipitate is then filtered off as before; care is again necessary, as the calcium oxalate, like barium sulphate, passes easily through filter paper. The precipitate is washed by decantation, and also when on the filter, with very dilute cold ammonia solution. It is then dried in the steam oven. The calcium oxalate may be treated in either of two ways, of which that first given below is to be preferred if a sufficiently powerful burner is obtainable.

1. The calcium oxalate and filter are transferred to a weighed crucible, and ignited strongly in a muffle furnace, or very powerful bunsen burner. This gives quicklime, CaO.

2. The ignition of the precipitate is performed by an ordinary burner, and after all the carbon from the filter paper has disappeared, the crucible is allowed to cool, solid pure ammonium carbonate is added, and the whole gently heated until no more ammonia comes off. The residue is calcium carbonate.

Result may be tabulated thus :—

Weight of calcium carbonate taken . . . $= m$

Weight of crucible . . . . $= d$

Weight of crucible $+$ CaO $+$ ash . . . . $= b$

or Weight of crucible $+$ CaCO$_3$ $+$ ash . . $= b'$

Weight of ash . . . . $= c$

Percentage of Ca $= \dfrac{40}{56} \times (b - a - c) \times \dfrac{100}{m}$

or $\qquad \dfrac{40}{100} \times (b' - a - c) \times \dfrac{100}{m}$

ESTIMATION OF IRON IN THE FERRIC STATE BY PRECIPITATION AS HYDROXIDE.

The ferrous ammonium sulphate prepared by the student may be used.

Weigh out about 1·5 grams of ferrous ammonium sulphate and dissolve it in about 100 c.c. of distilled water, with the addition of 5 c.c. concentrated sulphuric acid, add concentrated

nitric acid a few drops at a time, warming the solution, until a clear brownish-yellow liquid is obtained.   The oxidation is accompanied by the evolution of nitric oxide gas.

Add ammonium hydroxide as long as a precipitate is produced and until the liquid is alkaline, boil until there is only a slight odour of ammonia, wash several times by decantation, transfer the precipitate to a filter paper, wash again several times with hot water until the washings do not affect litmus paper and give no precipitate with barium chloride.

Dry the precipitate in the steam oven, and then transfer to a crucible in the manner described under the estimation of copper.   Burn the filter paper, ignite the precipitate and filter ash in the crucible, and weigh.

The calculation is similar in nature to that for copper as oxide.

ESTIMATION OF CARBON DIOXIDE IN CARBONATES.

This estimation is generally made by finding the loss in weight produced by the action of dilute hydrochloric acid upon the carbonate, the loss in weight being due to the escape of the carbon dioxide.   Care must, however, be taken to dry the gas which escapes, or otherwise the loss will be too great owing to the fact that not only carbon dioxide but water also will have been given off.   The various forms of apparatus which are found in use simply differ in the means adopted for drying the gas, and for preventing the gas from escaping before passing through the drying agent.

The method which stands first of those given below involves the use of no apparatus which the student cannot easily fit up for himself, and he is advised to do this.

A small wide-mouthed flask is fitted with a cork perforated with one hole, as shown in Fig. 16, and about one-third filled with dilute hydrochloric acid.   Into the hole in the cork is placed the small end of a drying tube filled with fused calcium chloride in small lumps : to prevent the calcium chloride from falling down

into the flask below, the lower part of the bulb of the drying tube is loosely plugged with glass wool, or asbestos. The carbonate to be analysed is put in a small glass tube closed at one end, too long to lie flat in the flask, but of such a length as to remain in a slanting position, as shown in the photograph, the mouth being above the level of the dilute hydrochloric acid in the flask.
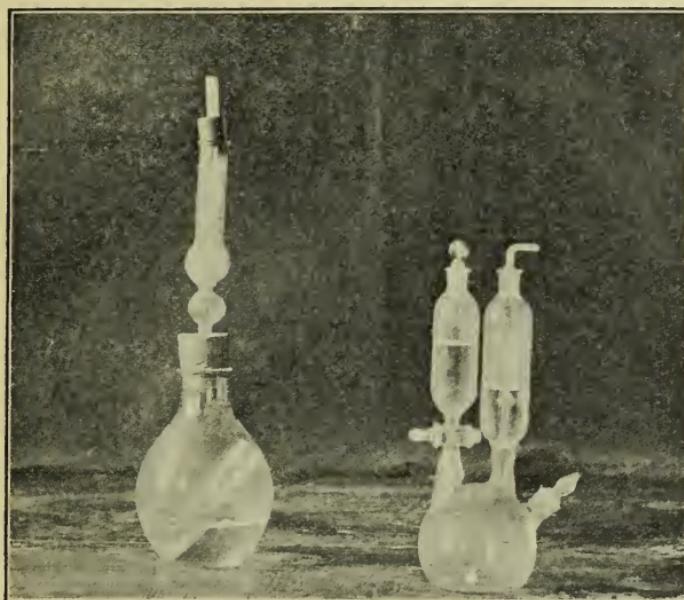

FIG. 16.

The following weights are taken :—

(*a*) Weight of flask + calcium chloride tube
    + hydrochloric acid + tube for holding
    carbonate . . . . = *a*   grams.

(*b*) Weight of same after introducing a con-
    venient quantity (say about 1 gram) of
    carbonate into the small tube . . . = *b*   ,,

Weight of carbonate taken . . . . . = *b* − *a*   ,,

(*c*) Weight of whole apparatus after escape
    of carbon dioxide . . . . . . = *c*   ,,

Loss in weight due to escape of CO_2 . . = *b* − *c*   ,,

The amount of carbon dioxide present in

$b - a$ grams of carbonate . . . . . . $= b - c$ grams,

And therefore the amount in 100 grams,

i.e. the amount per cent. . . . . . $= \dfrac{(b - c) \times 100}{b - a}$

With the above apparatus, in order to cause the acid to act upon the carbonate, it is necessary to incline the flask until the level of the acid is above the mouth of the small tube containing the carbonate, when the acid will descend into the small tube and evolution of gas will commence. Before weighing after the action of the acid on the carbonate, the apparatus should be gently warmed.

For practice, the student could not use a more convenient substance than Iceland spar (calcium carbonate), in small clear pieces.

A more satisfactory apparatus is that devised by Schrötter, also shown in Fig. 16.

The drying agent used is concentrated sulphuric acid, which is placed in the double tube shown on the right side of the apparatus in the photograph; the dilute hydrochloric acid is contained in the other tube, and can be allowed to run down into the flask on to the carbonate below by turning the tap. The weighings necessary, and the calculation from the observed weights, are the same as in the case of the use of the previously described apparatus, but some modifications of the method of working are introduced for the sake of greater accuracy.

The chief of these consists in expelling the carbon dioxide from the apparatus at the close of the reaction by gently heating the solution, and, whilst hot, drawing a current of air through the whole apparatus by opening the tap, removing the stopper, and sucking through a flexible rubber tube attached to the small exit tube.

As this is liable to remove also some hydrochloric acid gas, it is better to employ dilute sulphuric acid for dissolving the carbonate where this is possible; where, however, the carbonate is not easily attacked by sulphuric acid, hydrochloric acid may

be employed, and an absorption tube filled with pumice soaked in copper sulphate solution is then fitted to the exit tube, and weighed, of course, as part of the apparatus throughout. If the quantity of dilute hydrochloric acid is only slightly in excess of the amount neutralised by the carbonate, the error due to the loss of hydrochloric acid gas is small and may often be neglected if the solution is only heated on a water-bath, and thus not raised quite to the boiling point. The apparatus must be allowed to cool completely, and the tap must be opened before the final weighing, so that the bulb may be finally full of air at the atmospheric pressure ; the levels of sulphuric acid in the double tube are equal when this is the case.

Schrötter's apparatus is not an easy instrument to use, and, whilst it is much the more accurate in experienced hands, the student will probably find that he can obtain no better results with it than with the simpler form first described, which is, of course, quicker and easier in working.

STUDY OF SOLUBILITY OF SALTS
IN WATER

DETERMINE the solubility of the given salt at temperatures of 0°, 15° (or the room temperature), 30°, 45°, 60°, 75°, and 100°, according to the following methods :—

(1) At 0° C.,

Into a flask of 250 c.c. capacity place 150 c.c. of water, and add an excess of the powdered salt. Immerse the corked flask and its contents in powdered ice, and allow to remain at this temperature for a considerable time, if possible, three or four hours, shaking well every fifteen minutes. Decant off about 50 c.c. of the *clear* solution, taking care to avoid presence of any of the solid material, place in a deep crucible, which has been previously weighed, and weigh as rapidly as possible ; then cautiously evaporate to dryness, first on the water bath, and finally in the steam oven. Weigh the dish and residue ; the difference between this and the weight of the dish gives the weight of salt in the weighed quantity of the solution. Calculate the amount of salt dissolved by 100 grams of solvent.

(2) Repeat the experiment at the ordinary temperature, immersing the flask in a large vessel of water which has attained a steady temperature.

(3) At the temperature of boiling water.

Repeat the experiment, placing the flask in a water bath heated to boiling, noting the exact temperature of the water in the bath.

(4) For other temperatures, the principle of the method is the same, but it will be found convenient to immerse the flask in a

bath of rape oil kept at constant temperature by means of a thermostat. Calculate the solubility as before.

Plot the results on squared paper, using the temperatures as abscissæ and the solubilities as ordinates. Join the points.

Salts recommended for illustration of the method are : Potassium nitrate, lead nitrate, lead chloride, potassium dichromate, common salt, and calcium benzoate.

ELEMENTARY SPECTROSCOPIC WORK

THE most convenient form of instrument for chemical purposes is a direct vision spectroscope, as very little adjustment is necessary ; all that is required is to make the slit as narrow as the intensity of the light will permit, and focus by means of the sliding tube.

To examine the spectrum of a volatile salt, introduce into the flame of a bunsen burner the looped end of a platinum wire which has been dipped in a solution of the salt. The wire must be thoroughly cleaned before it is used for this purpose, as otherwise the spectrum obtained will always be mixed with those of the impurities upon the wire. Hold the spectroscope with the slit vertical at a distance of about two inches from the bunsen flame, and examine, by means of the eyepiece, the spectrum of the light emitted by the flame, which will be chiefly that of the incandescent salt, or of one of its constituents, superimposed upon a very faint continuous spectrum due to the feeble luminosity of the bunsen flame. In order to become familiar with the spectra of some of the metals the student should prepare a series of solutions of their chlorides, as these are generally more volatile than other salts, and keep each separately in a corked bottle, through which a piece of glass tubing, in which is mounted a platinum wire, is passed. The platinum wire is never used for any other solution than the one in which it is immersed.

The metals whose spectra may be examined in this simple manner, are sodium, potassium, lithium, (rubidium, cæsium), barium, strontium, calcium, thallium, and certain other rare metals, and the student is advised to prepare solutions of the chlorides of the more common of these, that is the metals of the alkalis and

alkaline earths, and examine them in the manner described above. The spectra of these metals are as follows :—

> *Sodium.* One bright yellow line (separable by a spectroscope of high dispersive power into two lines).
>
> *Potassium.* One line in the extreme red and one in the extreme violet.
>
> *Lithium.* One bright line in the red (and a much feebler orange-yellow line. Not seen under ordinary conditions).
>
> *Barium.* A series of yellow and green bands.
>
> *Strontium.* Orange bands, two red lines, one blue line.
>
> *Calcium.* Orange band, green band, feeble violet line.
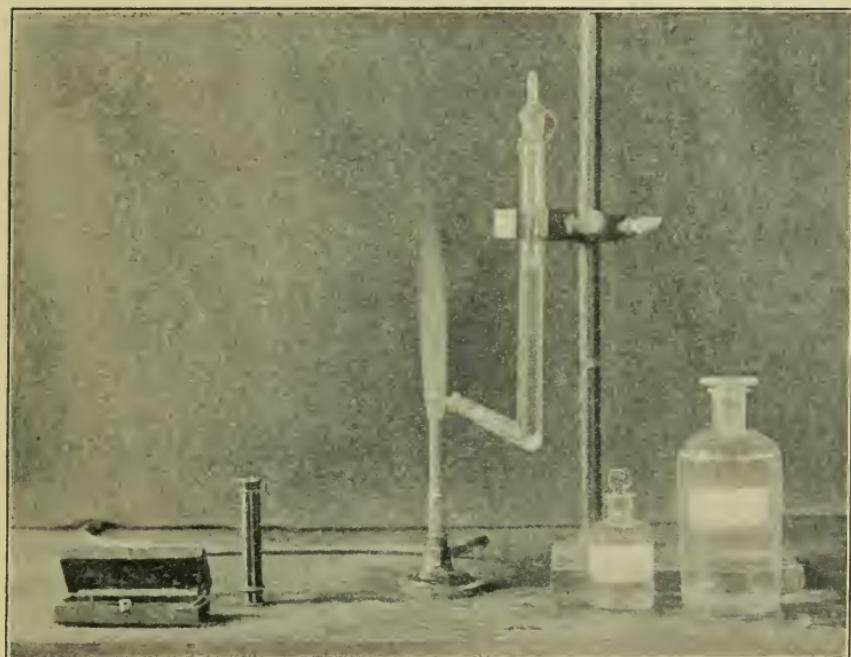
FIG. 17.

The flame coloration produced by the method we have described is not very lasting, and the method cannot be used for a continuous illumination. When this is necessary the apparatus designed by Mitscherlich may be employed ; it is shown in use in Fig. 17.

An ordinary Cowper's tube is closed with a cork at its lower end, and through the cork is passed a small wick made of a bundle of very fine platinum wires or asbestos threads. The tube contains a solution of the salt to be examined mixed with ammonium acetate, this latter compound causing the solution to flow more readily along the wick ; a convenient solution is made by mixing one volume of a saturated solution of the salt whose spectrum is required with 20 volumes of a 15 per cent. solution of ammonium acetate.

When the wick is placed in the bunsen flame, the solution passes slowly along it and is volatilised by the flame, imparting a persistent coloration.

QUALITATIVE ANALYSIS

Note.—The plan adopted in this scheme of qualitative analysis is in the nature of a compromise. If the student is supplied with tables ready made for the detection of the basic and acidic radicles, he is apt to fall into a purely mechanical habit of working, with the result that he becomes incapable of attacking problems in which any interference with the customary routine occurs. On the other hand, if the student is allowed to find out the reactions entirely on his own initiative, he frequently fails to appreciate the importance of method, which is as essential as a thorough understanding of the chemical principles involved.

The group reagents have, therefore, been specified in each case, with the reasons for their adoption : then follow the most useful confirmatory tests, but the student has been left to find out when visible reaction occurs, and what that reaction is. From the results of his own observations he should draw up a table, as shown in outline below.

The completed tables are sufficient for the determination of any simple salt, but if a complete separation is required, a much more elaborate procedure than falls within the scope of the present work is generally necessary. It will be found, however, that the student will derive much benefit from working out, from the tables he has drawn up, methods for demonstrating the presence of each of two metals in the same, as well as in different, groups. One of the more difficult cases, that of tin and antimony, is given below under Group 2, as a guide to the way in which such problems may be attacked.

In using the tables, after his completion of them, for the detection of unknown substances, the student should carefully enter in his note-book particulars of each experiment, its result, and his inference therefrom, before commencing the next experiment.

PRELIMINARY EXAMINATION OF THE SUBSTANCE.

These observations will be found useful as indicating in many cases the presence of elements or groups which either interfere with the normal reactions as given by the substances in solution, or are liable to be overlooked, unless these preliminary tests are performed. Examples of the former class are afforded by the salts of organic acids, and of the latter by nitrates.

It is not, however, always safe to come to a definite conclusion on the strength of these observations, but the information they afford should be carefully noted and used in conjunction with that given in the subsequent examination of the dissolved substance.

The chief of these "dry" reactions are given below, with some indication of the things to be observed : the student should try the behaviour of all the more common substances, but the table in this case can be amplified in the course of practice, the results obtained with each fresh substance being incorporated as occasion requires.

Test 1. Character of substance : colour, crystalline form, if any, deliquescence, efflorescence, hardness, etc.

Test 2. Solubility in water.

Test 3. Treat the solid substance with dilute hydrochloric acid. Identify any gas which may be evolved.

Test 4. Treat the solid substance with concentrated hydrochloric acid : heat, if necessary. If an oxidising agent is present, chlorine will be evolved (*e.g.* peroxides).

Test 5. Treat a small quantity of the solid substance with concentrated sulphuric acid : heat, if necessary.

Record :—

> (I) Substances which give off a volatile acid,
>> (*a*) with decomposition of the volatile acid (*e.g.* iodide, chlorate);
>> (*b*) without decomposition of the volatile acid (*e.g.* chloride).
>
> (II) Substances evolving carbon dioxide and monoxide, either or both, and with or without charring.

Test 6. A small quantity of the substance is heated in a small test-tube. The following should be recorded :—

> (*a*) Substances which yield a sublimate and the appearance of the sublimate.
>
> (*b*) If there is a sublimate, repeat the heating in the tube, having previously mixed the substance with dry sodium carbonate.
>
> (*c*) Substances which give off a gas and the chemical nature of the gas (O_2, CO_2, NO_2, etc.).
>
> (*d*) Substances which give off water and the reaction of the water to litmus.
>
> (*e*) Substances which decrepitate.

Test 7. A small quantity of the substance is heated on charcoal in the reducing flame of a mouth blowpipe. The following should be recorded :—

I. Oxides and salts yielding metal

> (*a*) with incrustation ;
>
> (*b*) without incrustation.

>> **Note.**—Incrustations are formed if the metal is volatile at the temperature of the flame, when it is carried forward into the oxidising portion of the flame, oxidised, and the oxide deposited on the cooler part of the charcoal. The colour of the incrustation often affords valuable information as to the metal present. The character of the metal obtained should be noted, or this may be left till the product of Test 8 is examined.

II. Compounds which give off oxygen when heated and consequently cause deflagration.

III. Compounds which melt and sink into the charcoal.

IV. Compounds which leave a white infusible residue.

Test 8. A small quantity of the substance is mixed with four or five times its bulk of dry sodium carbonate and the mixture is heated on charcoal as before.

Any metal which is obtained should be examined, and special note made of its colour, hardness, malleability, and the effect of the **clean** metal on writing-paper.

Test 9. If a **white** infusible residue is obtained in 7, add a couple of drops of cobalt nitrate solution to the residue and again heat strongly.

Certain compounds give characteristic colours.

It is necessary to heat for several minutes, as otherwise one is apt to obtain a blue colour from dehydrated cobalt salt which is not yet decomposed to oxide.

Test 10. If the residue in Test 7 is **not white,** heat a very small quantity of the substance in a borax bead.

The compounds of certain metals dissolve in fused borax, imparting to it a characteristic colour. (It is worth noting that the same metals are used to impart similar colours to glass.)

EXAMINATION OF THE SUBSTANCE IN SOLUTION.

After examining an unknown substance by the preliminary tests, the student should make a solution of the substance and proceed in the manner suggested on pp. 99 *et seq*.

In the following pages, the scheme for the detection of the acid radicles is placed first, but it is intended that the teacher should use his discretion as to whether the student should become familiar with these reactions before compiling his tables for the metals. The advantage of the order here given is that, as in

certain cases it happens either that the precipitation of a metal is prevented by the presence of an acid radicle, or that the acid itself produces a precipitate which may be mistaken for one indicating the presence of a metal, it often saves time and trouble if the acid radicles are first discovered. On the other hand, the detection of the metal radicles, when combined with the simpler acids, is more systematic and easier for an inexperienced student, and there is much to be said for the plan of allowing a student first to make up his tables for the metals using such salts, then to compile his acid tables, and finally to return to the metals using the "complicating" acids. In detecting an unknown substance, it is advantageous to conduct the tests for the detection of acids concurrently with those for the detection of metals.

The acidic radicles most likely to cause mistakes are—

(1) Thiosulphate, which gives a white or yellow precipitate with hydrochloric acid, or indeed any acid.

(2) Certain organic acid radicles which prevent the precipitation of iron by ammonia.

(3) Oxalates, phosphates, fluorides, borates of the alkaline earth metals which are precipitated on the addition of ammonia in Group 3 (metals).

The preparation of the solution needs a few remarks. If the substance dissolves in water, this solution will usually serve for the detection both of the acidic and of the basic radicles. In testing for the acids, when the substance is not soluble in water, a solution in nitric acid may be used for one division of the silver nitrate group, and a hydrochloric acid solution for the barium chloride test. It will be seen, however, that a neutral solution is required for some important reactions, and an alkaline one for another series. It is, therefore, more satisfactory, if the substance does not dissolve in water, or if its aqueous solution gives a precipitate with ammonia, to boil some of the substance with a concentrated solution of sodium carbonate, and filter. The filtrate is made distinctly acid with nitric acid and boiled to expel the carbon dioxide. Ammonia is then added in very slight excess, and the solution once more boiled until all the

H

excess of ammonia is driven off. The neutral solution so obtained
is then used for the acid tests as given in detail on pp. 99 *et seq.*

Note.—If it is necessary to fuse the substance with fusion mixture in order
to test for the metals (see below), the water extract from the fusion is used for
testing for the acids, being treated in exactly the same way as the filtrate from
the boiling with sodium carbonate solution above.

For the detection of the metals, if the substance does not
dissolve in water, the student should try dilute hydrochloric acid ;
if this is successful, the solution may be used, in the absence of
phosphates, oxalates, etc. (see p. 112), for the detection of the
metals, as in the tables following. If the substance does not
dissolve in dilute hydrochloric acid, concentrated hydrochloric
acid may be tried, heating if necessary, but as little as possible
of the concentrated acid should be used, and the solution so
obtained must be diluted before going further. It is not generally
convenient to make a solution in nitric or sulphuric acids, or
in aqua regia, although certain substances can advantageously be
treated with one or other of these acids. For example, many
alloys must be dissolved in nitric acid, whilst certain organic
compounds not soluble in water or hydrochloric acid are decom-
posed readily by sulphuric acid.

If, therefore, the substance to be analysed does not dissolve
in water or hydrochloric acid, it is generally better to fuse at once
with fusion mixture.

For the fusion, the dry substance should be mixed with four
or five times its bulk of dry fusion mixture—sodium and potassium
carbonates in equimolecular proportions (see p. 117)—and heated
in a platinum capsule[1] to a bright red heat, and maintained at a
temperature well above the melting point of the fusion mixture
for twenty minutes. The capsule and its contents are then
allowed to cool, and the solid mass extracted several times with
boiling water ; or the capsule may conveniently be placed in a
beaker of water and the water boiled for some minutes. The
solution is then filtered, and the residue washed thoroughly with

---

[1] Platinum must not be used if metals are present (*e. g.* lead) which alloy
with platinum. In such cases porcelain or nickel should be used.

boiling water. The filtrate is used for testing for the acids in the manner given above, whilst the residue is dissolved in dilute hydrochloric acid, and used for the metal tests, any residue insoluble in hydrochloric acid being examined for metals of Group I (Pb, Ag, Hg').[1]

Fusion mixture does not give satisfactory results with a few substances, of which the most important are calcium phosphate, calcium fluoride, and certain complex cyanides. Calcium phosphate is soluble in dilute hydrochloric acid, but is re-precipitated by ammonia. Directions for treatment are given on p. 112.

Calcium fluoride is best treated with concentrated sulphuric acid (*cf.* p. 113).

Complex cyanides are also decomposed by evaporation to dryness with concentrated sulphuric acid.

If tartrates or citrates are present iron and aluminium will not be precipitated by ammonia, and it may be an advantage to remove these by evaporation with concentrated sulphuric acid, as in the case of cyanide.

(A) ACIDIC RADICLES.

Group I.

(a) Acids needing no further tests than those already given as " preliminary : " carbonate, chlorate, hypochlorite, sulphide.

(b) Acids already indicated, but of which further confirmation is necessary :

Sulphite, see p. 101.

Nitrite and Nitrate, see p. 102.

Tartrate, citrate, oxalate, fluoride, see Group III.

Chloride, bromide, iodide, thiosulphate, see Group IV.

[1] The following metals form water-soluble compounds on fusing with fusion mixture, and must be tested for in the aqueous extract : aluminium, chromium, zinc, manganese, arsenic, and tin. Of these chromium, manganese, and arsenic form acidic radicles which will be detected in the usual routine ; the others will be converted into their ordinary salts on neutralising with hydrochloric acid, and must be detected by the tables for basic radicles.

Group II.

	Ferro-cyanide.	Ferri-cyanide.	Thio-cyanate.	Acetate.	Phosphate.	Arsenate.
To neutral solution add— (1) Ferric chloride sol. . .						
(2) Ferrous sulphate sol. .					●	

Group III.

	Sulphate.	Phosphate.	Arsenate.	Borate.	Tartrate.	Citrate.	Oxalate.	Fluoride.
To neutral solution add barium chloride sol. .								
Add HCl to precipitate .								
To neutral solution add calcium chloride sol. .								
To precipitate add acetic acid					.			

Group IV.

	Chloride.	Bromide.	Iodide.	Cyanide.	Ferro-cyanide.	Ferri-cyanide.	Thio-cyanate.	Phosphate.	Arsenate.	Thio-sulphate.
To neutral solution add silver nitrate sol. . .										
Ppt. + HNO₃ (dil.) . .										
Ppt. + NH₃ sol. . . .										
If precipitate dissolves in NH₃, make again acid with HNO₃										

There are a few acidic radicles which are apt to be missed, and it is necessary to test for these by means of the following special reactions. The presence of some of these acids will have been already suspected, and it is only necessary to confirm previous indications.

Chromate.—The presence of chromates is suggested by yellow or orange colour, and will be further indicated by the action of sulphuretted hydrogen upon the acid solution (p. 110), as well as by the silver nitrate reaction. A useful confirmatory test is to treat some of the solid with alcohol and concentrated sulphuric acid. On warming, the characteristic smell of aldehyde is obtained. Hydrogen peroxide imparts a deep blue colour to the solution of the chromate in the presence of a mineral acid. The colouring matter is soluble in ether, but rapidly decomposes and evolves oxygen with effervescence.

Permanganate.—This is almost sufficiently revealed by its purple-crimson colour, and by its giving a precipitate of sulphur in Group 2 of the metal tests.

It may be confirmed by pouring a few drops of a dilute solution into oxalic acid dissolved in water, with the addition of a little sulphuric acid, and warming. The crimson solution is decolorised, and carbon dioxide is evolved.

Sulphite.—Sulphites give off sulphur dioxide when treated with hydrochloric acid, but it is easy to overlook this. The presence of sulphite may be confirmed by treating the solid with zinc and dilute hydrochloric acid, when sulphuretted hydrogen is evolved.

Cyanide.—Cyanides give a precipitate with silver nitrate solution, but the precipitate of silver cyanide is as soluble in ammonia as silver chloride. It is therefore necessary to apply further tests. Add to the original solution caustic soda till strongly alkaline, then freshly prepared ferrous sulphate solution, and boil. Now add ferric chloride solution, and finally excess of hydrochloric acid: a blue or green precipitate or coloration indicates cyanide.

The silver cyanide is also distinguished from the chloride by

the fact that it is completely decomposed by boiling for some time with dilute nitric acid, whereas the chloride is not affected by this treatment. This process enables one to distinguish chloride in presence of cyanide, but it is tedious.

Nitrate and Nitrite.—These will have been given by the preliminary tests, but it is well to confirm by the " brown ring test."

A solution of the substance in water is divided into two parts. To one portion a little *dilute* sulphuric acid is added, and some of a freshly prepared solution of ferrous sulphate made with cold water. If a nitrite is present there will be a brown coloration where the two solutions meet, which rapidly spreads to the whole of the liquid. On warming a brisk evolution of nitric oxide occurs, and the solution acquires a clear red-brown colour.

The other portion of the solution is cooled, if necessary, and some of the freshly prepared solution of ferrous sulphate added. Concentrated sulphuric acid is then poured slowly down the side of the test-tube (which is held in a slanting position), so as to form a layer at the bottom of the tube without disturbing or mixing with the solution. If a nitrate is present a brown ring will be formed at the junction of the two liquids. Nitrites give the same reaction, but the " ring " usually quickly spreads to the rest of the solution. If a brown ring is obtained, it is necessary to prove the absence of nitrites by means of the test given above and with hydrochloric acid (in the preliminary examination), before concluding that a nitrate is present.

Silicate.—A solution of the silicate on evaporation with hydrochloric acid gives an insoluble residue (several evaporations with fresh quantities of concentrated acid are generally necessary). This residue can be further tested by placing a small quantity on a bead of microcosmic salt, and heating in the blowpipe flame. Silica is indicated by the appearance of small infusible specks floating in the molten bead.

Borate.—Some of the solid substance is heated with about 10 c.c. of concentrated sulphuric acid in a small evaporating basin. After cooling to a moderate temperature, about 20 c.c. of

alcohol is poured into the mixture and set on fire. The mixture may be gently heated for a few minutes, but this is usually unnecessary. If a borate is present the flame shows a brilliant green edge.

The following is an interesting and effective modification of this method of demonstrating the presence of a borate :—

To the solid salt add concentrated sulphuric acid and methyl alcohol (purified wood spirit), and distil. The distillate is methyl borate with excess of methyl alcohol; when this mixture is burnt, the green colour imparted to the flame is very brilliant.

Borates moistened with hydrochloric acid impart a brown colour to turmeric paper, which becomes dark green on the addition of caustic soda (*cf.* p. 36).

Fluoride.—When heated with concentrated sulphuric acid, fluorides give a characteristic appearance, as if oily drops were rising through the sulphuric acid. Further, if a wet glass rod be held in the gas evolved, it will become coated with a white deposit of silica. To obtain this reaction, it is better to mix the fluoride with an excess of silica, heat with concentrated sulphuric acid, and lead the evolved gas into water (*cf.* p. 31). A thick white deposit of silica is formed (see p. 32).

Phosphate.—The substance should be dissolved in nitric acid, as the presence of hydrochloric acid interferes with the delicacy of this test; a solution of ammonium molybdate (p. 117) is then added, and the mixture gently warmed. The temperature should not exceed 60° C., as on boiling a yellowish-white precipitate of molybdic acid is given, which may be mistaken for the yellow precipitate due to phosphate. Arsenates give a similar precipitate, but can be distinguished from phosphates by their reaction with sulphuretted hydrogen (see p. 110).

Detection of More than One Acid in a Mixture.

The tests given above, if intelligently performed, will be sufficient in many cases, even where the two acids are in the same group. Thus, for example, if the student were examining a

mixture of the sodium salts of citric and boric acids, a white precipitate would be obtained with calcium chloride, soluble in acetic acid. This may be, however, due to either or both of these radicles; but citrates give a characteristic reaction with concentrated sulphuric acid (though this is very similar to that for tartaric acid, see below), whilst the presence of borate is shown by the special green flame reaction.

Two cases need special consideration, (1) a mixture of tartrate and citrate, and (2) chloride, bromide, and iodide, if two or more be present in the mixture.

Tartrate and Citrate.—With each of these calcium chloride yields a white precipitate soluble in acetic acid, the calcium tartrate rather more easily than the citrate. When treated with concentrated sulphuric acid they each char and give off carbon monoxide, but the charring takes place more slowly with the citrate than with the tartrate. This slight difference may be sufficient in experienced hands to determine the presence of either acid in the absence of the other.

The presence of tartrate may be confirmed as follows: To a moderately concentrated solution of silver nitrate, add caustic soda as long as a precipitate is produced, allow to settle, pour off the clear liquid, and dissolve the solid residue in ammonia. To this add the neutral solution of the substance which is being examined, and warm gently: the presence of the tartrate will be shown by a brilliant silver mirror upon the sides of the test-tube.

Chloride, Bromide, and Iodide.—In this case a series of additional reactions is given, and it will be a good exercise for the student to devise a scheme for the detection of each of these radicles in a mixture containing all three, by means of these reactions and those previously given, as he will now have at his disposal, not only those reactions which are common to these three halogen acids, but also some which are special to each.

	Chloride.	Bromide.	Iodide.
Mix solid with powdered $K_2C_2O_7$ and H_2SO_4, and pass the evolved gas into water, to which then add lead acetate solution			
To the solution— (1) Add chlorine water and a small quantity of chloroform			
(2) Add bromine water and chloroform			
(3) Add copper sulphate + solution of sulphur dioxide			
(4) Add lead acetate, then boil and allow to cool .			
(5) Add potassium nitrite, dilute acetic acid, and starch solution			

(B) BASIC RADICLES.

Group 1.—Metals the chlorides of which are insoluble in water or acids.

GROUP REAGENT: *dilute hydrochloric acid.*

	Silver.	Lead.	Mercury(ous).

1. To solution add HCl . . .
    (*a*) To precipitate add boiling water . . . .
    (*b*) To precipitate add dil. NH_3 . . . . . .
	White precipitate.	White precipitate.	White precipitate.

2. Original solution (neutral) + KI sol.			
3. Original solution (neutral) + K_2CrO_4 sol.			
4. Original solution + NaOH first in small quantity and then in excess			
5. Original solution + Na_2CO_3 in excess			

NOTES.

1. When tests 2 to 5 are applied to the original solution the reactions may be complicated by the presence of a metal belonging to a later group, and the appearance of the precipitate may be somewhat abnormal, but the reasons for this will become clear during the ordinary course of the analysis.

2. If the hydrochloric acid is concentrated, barium salts are precipitated ; if the acid is very dilute, bismuth oxychloride may be precipitated, which, however, dissolves on the addition of a few drops of concentrated acid.

3. Thiosulphates and polysulphides yield a white to yellow precipitate of sulphur, but the appearance of this will soon be easily recognised.

If there is no precipitate in this group, proceed with the same solution to the next group. If a precipitate is obtained, filter it off, and wash with cold water. Proceed to the next group with the filtrate, and examine the precipitate by Tests 1 (*a*) and 1 (*b*) above.

Exercise.—By the aid of the above reactions, separate and demonstrate the presence of each of the metals in a mixed solution of the nitrates of silver, lead, and mercury(ous).

Group 2.—Metals the sulphides of which are precipitated in the presence of dilute hydrochloric acid.

Note.—If the acid is too concentrated, certain sulphides (*e.g.* those of bismuth and cadmium) will not be precipitated here.

Group Reagent: *dilute hydrochloric acid + sulphuretted hydrogen.*

To Filtrate from Group 1, add:—	Pb.	Hg''.	Cu.	Bi.	Cd.	Sn^{iv}.	Sn''.	Sb.	As.
1. Dil. HCl + H₂S	Black ppt.	Black ppt.	Dark brown ppt.	Black ppt.	Bright yellow ppt.	Dull yellow ppt.	Dark brown ppt.	Orange ppt.	Bright yellow ppt.
(a) Precipitate from 1 + boiling (NH₄)₂S	Insol.	Insol.	Insol.	Insol.	Insol.	Sol.	Sol.	Sol.	Sol.
(b) Precipitate from 1 (*after washing free from* H₂S) + (NH₄)₂CO₃ sol.									
(c) Precipitate from 1 + NaOH sol.									
(d) If precipitate dissolves re-acidulate solution (for a, b, and c)									
(e) Precipitate from 1 + boiling conc. HCl									
(f) Precipitate from 1 + boiling HNO₃ (sp. gr. = 1·2)									

2. NH₄Cl sol. + excess of water								
3. NH₄OH sol. and in excess								
4. After nearly neutralising, + KI sol., first in small quantity and then in excess								
5. HgCl₂ sol.								
6. NaOH sol., first in small quantity and then in excess								
7. Excess Na₂CO₃ sol. . .								
8. HCl + Zn, followed by HgCl₂ sol. . .								
9. HCl and Cu								
10. K₄Fe(CN)₆ sol. . . .								

NOTES TO GROUP 2.

(1) If any oxidising agent is present in the solution (*e.g.* ferric compounds, chromates), a white or pale yellow precipitate of sulphur will be obtained, which usually passes easily through the filter paper and can be thus distinguished from the other precipitates. Two cases are of special interest : if a yellow solution, orange after the addition of HCl, gives with H_2S a precipitate of sulphur whilst the colour of the solution turns green, a chromate is present. This is a very useful indication, as chromates are easily missed (see p. 101). The second case is that of arsenic as arsenate : here sulphur is first precipitated, and only when the whole of the arsenate has been reduced to arsenite is a precipitate of sulphide of arsenic obtained. In all cases, therefore, where a precipitate of sulphur occurs, sulphuretted hydrogen should be passed through the solution for some time, with occasional boiling, in order to ensure the detection of arsenic, if present.

(2) If the hydrochloric acid is in great excess, sulphuretted hydrogen precipitates lead as sulpho-chloride ($PbCl_2$. PbS), which is brownish-red in colour. On the addition of water, however, this compound is decomposed, and, in the presence of sulphuretted hydrogen, lead sulphide is formed.

(3) Mercuric salts also undergo a somewhat similar change under the influence of H_2S, a white chloro-sulphide being first produced, but this rapidly becomes yellow, then brown, and ultimately black on the continued passing of H_2S, without any further precautions being taken.

(4) Another consequence of excess of hydrochloric acid is the prevention of the precipitation of Bi and Cd.

Suggestions for using the above table for the detection of tin and antimony compounds in a mixed solution. (See remarks on p. 93.)

1. The precipitate with HCl $+ H_2S$ is digested with boiling $(NH_4)_2S$. It is found to be completely soluble. Hence Cd,

Bi, Cu, Hg, Pb are absent, and solution contains one or more of As, Sb, Sn'', Sn^{iv}.

2. Digest a further quantity of the H_2S precipitate (after washing free from H_2S) with $(NH_4)_2CO_3$ solution, and filter. Acidify filtrate : no yellow precipitate (or only a little sulphur), absence of As.

3. Orig. sol. $+ HgCl_2$: no effect, Sn'' absent.

4. Orig. sol. $+ Zn +$ conc. HCl ; when all zinc has dissolved $+ HgCl_2$: white precipitate, turning grey, indicates (in conjunction with 3) Sn^{iv} in original solution.

5. Orig. sol. $+ Cu +$ HCl : grey deposit indicates As or Sb. But As is absent, so Sb is present.

6. Orig. sol. $+ NH_4Cl +$ excess of water : white precipitate confirms Sb.

If no precipitate is obtained in Groups 1 and 2, proceed with the original solution as below : if, however, a precipitate has been obtained in the preceding group, the filtrate should be boiled for a few minutes, a couple of drops of concentrated nitric acid added, and the solution again boiled before passing on to Group 3. The addition of the nitric acid helps to get rid of the sulphuretted hydrogen (by oxidising it to sulphuric acid), and also oxidises any ferrous salt : ferric hydroxide is more easily and completely precipitated by ammonia than is ferrous hydroxide, whilst the original solution being used for Tests 6 and 7 of Group 3 will give information as to the kind of iron salt actually present. If a simple salt only is given, and no precipitate has been obtained, it is not necessary to add nitric acid to the original solution to oxidise the iron, though some prefer to do so in all cases, before adding ammonia.

If a precipitate of sulphur only has been obtained in Group 2, it is usually better to start afresh for Group 3, but if, in addition to the sulphur precipitate, there has been a change of colour from orange to green (indicating a chromate, see p. 110), it is advisable, perhaps, to filter off as much sulphur as possible and proceed with the filtrate, boiling off the H_2S, adding a few drops of concentrated nitric acid, and again boiling until the finely

divided sulphur is completely oxidised, or has become granulated and can be filtered off. Then the chromium will be precipitated as indicated below, and the presence of chromate in the original substance be confirmed. This method is not necessary, and it can be left to the experience of the individual student to deter- mine whether it is, to him, preferable to take a fresh portion of the original solution for Group 3 in this case also, and confirm the chromate by the ordinary acid table.

A further important point in connection with this third group is that certain substances which are soluble in dilute hydrochloric acid and insoluble in water are precipitated on the neutralisation of the acid by the ammonia. The most important of these are the phosphates, borates, fluorides, and oxalates of the alkaline earth metals, which come down as white precipitates. Silica is also occasionally precipitated as a white gelatinous precipitate. The metals properly belonging to this group may also be precipi- tated as phosphates. Therefore, if a white precipitate is obtained, it is necessary to test for phosphates, oxalates, etc., if these have not already been discovered in the preliminary investigation.

If a phosphate is present it can be eliminated in the following manner. The precipitate obtained by adding ammonium chloride and ammonia is dissolved in warm dilute hydrochloric acid, and nearly neutralised by the addition of sodium carbonate,[1] a mixture of sodium acetate[1] and acetic acid added, the solution boiled and filtered. The precipitate contains the phosphates of aluminium, chromium, or iron, and may contain the whole of the phosphoric acid. To the filtrate add ferric chloride drop by drop : the presence of more phosphoric acid is indicated by the yellowish-white precipitate (ferric phosphate), and as soon as precipitation is complete, the liquid assumes a distinctly reddish colour due to the formation of ferric acetate.

The mixture is diluted and gently boiled for some time, whereby the whole of the iron is precipitated as basic ferric acetate, which is filtered off and thrown away. The solution

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[1] If sodium salts are used, the presence of sodium in the original substance cannot, of course, be determined in the filtrate from this group.

may now contain the chlorides of the metals of Group 4 and subsequent groups, and is to be treated as shown in the tables for those groups.

The precipitate produced by sodium acetate and acetic acid is dissolved in dilute hydrochloric acid, and the tests in the table for Group 3 applied. The chief differences in the reactions will be found in Tests Nos. 1 and 2.

Fluorides and oxalates, which interfere with this group, are best removed by evaporation with concentrated sulphuric acid, the residual sulphates being dissolved by water or dilute hydrochloric acid.

Group 3. Metals, not occurring in any of the preceding groups, which are precipitated as hydroxides in the presence of excess of ammonium chloride.

GROUP REAGENT: *ammonium chloride + ammonia.*

To Filtrate from Group 2, add :—	Ferrous.	Ferric.	Aluminium.	Chromium.
1. NH_4Cl sol. (in excess) + NH_4OH sol.	Dark green ppt.	Red ppt.	Gelatinous white ppt.	Gelatinous pale green ppt.
2. (a) NaOH sol., first in small quantities and then in excess . . (b) And boil . . . . (c) If sol. obtained with NaOH, add NH_4Cl sol. in excess . .				
3. NaH sol. in excess + Br water and boil . . .				
4. Excess of Na_2CO_3 sol. .				
5. Original solution + $K_4Fe(CN)_6$ sol. . . .				
6. Original solution + $K_3Fe(CN)_6$ sol. . . .				

Filter off any precipitate, and proceed with the filtrate to the next group. It is advisable to add the ammonium sulphide, or sulphuretted hydrogen, to a small portion of the solution first. If there is no precipitate, that test portion can be thrown away, and the bulk of the solution used for Group 5 without adding any sulphide. If, on the other hand, there is a precipitate, ammonium sulphide (or sulphuretted hydrogen) must be added to the whole quantity of the solution. On the whole, sulphuretted hydrogen is to be preferred to ammonium sulphide, as it gives a cleaner pre-cipitate, without excess of sulphur, and does not impart a yellow colour to the filtrate. The precipitate produced by sulphuretted hydrogen or ammonium sulphide is more compact and more easily filtered if the solution is hot when the reagent is added.

Group 4. Metals, other than the above, which give sulphides, insoluble in alkaline solutions.

GROUP REAGENT : *ammonium chloride, ammonia, and sulphuretted hydrogen.*

To Filtrate from Group 3, add :—	Zinc.	Manganese.	Nickel.	Cobalt.
1. NH_4Cl sol. $+ NH_4OH$ sol. $+ H_2S$ (a) Precipitate from 1 $+$ dil. HCl . . (b) Precipitate from 1 $+$ aqua regia . .	White ppt.	Flesh-col-oured ppt.	Black ppt.	Black ppt.
2. NaOH sol., first in small quantities and then in excess				
3. NaOH sol. $+$ Br water .				
4. Na_2CO_3 sol. in excess .				
5. Sodium acetate conc. sol. $+ KNO_2$ conc. sol. in excess $+$ acetic acid in excess				
6. Borax bead test . . .				

After filtering off any precipitate obtained in the preceding group (see remarks at the head of Group 4), proceed to

Group 5. Metals (other than the above), the carbonates of which are precipitated in alkaline solutions.

GROUP REAGENT: *ammonium chloride, ammonia, and ammonium carbonate.*

It is advisable to add also a little ammonium oxalate, as this gives, in the case of calcium, a precipitate of oxalate which is less soluble than the carbonate.

To Filtrate from Group 4, add :—	Calcium.	Strontium.	Barium.
1. NH_4Cl sol. + NH_4OH sol. + $(NH_4)_2CO_3$ sol.	White ppt.	White ppt.	White ppt.
2. $CaSO_4$ sol.			
3. Dil. H_2SO_4			
4. Na_2HPO_4 sol.			
5. Dissolve precipitate from 1 in acetic acid and add K_2CrO_4 sol. If no precipitate, boil .			
6. Flame test			

After filtering off any precipitate proceed to

Group 6. Comprising magnesium, sodium, lithium, potassium, and ammonium. Divide the solution into two portions, and to one add sodium phosphate solution: a white precipitate is given by magnesium, and by lithium if the solutions are concentrated. (Lithium may also give a precipitate with ammonium carbonate if the solution is very concentrated.) Evaporate the other portion to

dryness and heat until fumes of ammonium salts cease
to be evolved, then

	Lithium.	Sodium.	Potassium.
1. Add solution of sodium cobalti-nitrite to concentrated solution of residue			
2. Add to concentrated solution of residue, solution of potassium antimonate			
3. Flame test			

INDICATORS AND REAGENTS

Phenolphthalein. One gram in 1000 c.c. dilute alcohol.

Methyl Orange. Half gram in 1000 c.c. water.

Litmus. Extract powdered litmus with boiling water. For a method of obtaining solution of the pure colouring matter of litmus, see " Sutton's Volumetric Analysis."

Ammonium Thiocyanate. One part in 100 parts of water.

Potassium Ferricyanide. Three parts in 100 parts of water.

Potassium Chromate. Cold saturated solution.

Starch Solution. Should be made by sprinkling a *very little* starch into 50 c.c. of boiling water, and boiling till the starch is dissolved. It is important that only a small quantity of starch be added : so called " starch paste " is quite unsuitable for the purpose of indicating iodine. The solution should be so dilute as to mix at once and completely with excess of water. It is very rare for the inexperienced to err in making the starch solution too weak, but very usual to make it too strong.

Fusion Mixture.—The most effective fusion mixture, in which the sodium and potassium carbonates are very intimately mixed, is obtained by calcining Rochelle salt (sodium potassium tartrate), lixiviating with water, and evaporating to dryness the solution thus obtained.

Ammonium Molybdate.—The powdered salt is dissolved in concentrated ammonia solution, and allowed to stand

for some time. A slight yellow precipitate containing
ferric hydroxide usually subsides. The clear liquid is
then poured into concentrated nitric acid as long as the
precipitate of molybdic acid which at first forms is
redissolved. The solution is ready for use after standing
for 12 hours.

Aqua Regia.—Prepared, when required only, by mixing one
volume of concentrated nitric acid with three volumes of
concentrated hydrochloric acid.

Bromine Water.—A saturated solution made by shaking
a small quantity of bromine with distilled water in a
stoppered bottle.

Calcium Hydroxide.—Lime Water. A saturated solution
made by mixing distilled water with slaked lime, allowing
the solid to subside, and syphoning off the clear liquid
when required.

Calcium Sulphate.—A saturated solution.

Mercuric Chloride.—A saturated solution made with hot
distilled water and allowed to cool.

Sodium Acetate and Acetic Acid.—Dissolve 34 grams of
the salt in 200 c.c. of water and add 50 c.c. of glacial
acetic acid.

Stannous Chloride.—Dissolve 112 grams of the salt in
100 c.c. of concentrated hydrochloric acid, diluted with
its own volume of water, and add water to the clear solu-
tion until the volume is one litre. The solution must be
kept over some fragments of metallic tin.

Potassium Antimonate.—Boil 1 part of potassium metan-
timonate with 12 parts of water for three hours and
filter. The solution should be clear and neutral. The
metantimonate is made by heating together 1 part of
finely powdered antimony with 4 parts of nitre, and
pouring the fused mass on to a stone slab. This
crude metantimonate may be powdered and used for
the preparation of the reagent, as above, without
any purification.

Sodium Cobaltinitrite.—Twenty-five grams of crystallised cobalt chloride, dissolved in 200 c.c. of water, mixed with a solution of 50 grams of sodium nitrite in 200 c.c. of water, and 100 c.c. of " twice normal " acetic acid added.

Other Reagents.—A convenient strength for all dilute solutions not otherwise mentioned will be " twice normal."

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THE END

Date Due